MXENE MODIFIED LAYERED DOUBLE HYDROXIDE NANOCOMPOSITE FOR PHOTOCATALYTIC CARBON DIOXIDE REDUCTION TO RENEWABLE FUELS

AZMAT ALI KHAN

A thesis submitted in fulfilment of the
requirements for the award of the degree of
Doctor of Philosophy

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

DECEMBER 2021

DEDICATION

This thesis is dedicated to my father for giving me strength to reach for the stars and chase my dreams, to my mother who always prayed for me and all other family members for their support

ACKNOWLEDGEMENT

First and foremost, praises and thanks to the Almighty Allah, for His showers of blessings throughout my research work to complete the research successfully.

I wish to express my sincere appreciation to my main supervisor, Dr. Muhammad Tahir, for encouragement, guidance, critics and friendship. I am also very thankful to my co-supervisor Dr. Ir. Zaki Yamani Zakaria for his support. Without their continued support and interest, this thesis would not have been the same as presented here.

My fellow postgraduate student should also be recognised for their support. My sincere appreciation also extends to all my colleagues and others who have provided assistance at various occasions. Their views and tips were useful indeed. I am grateful to my parents for their prayers. Also, I am thankful to wife for understanding, prayers and continuous support. I am also grateful to my brothers for their support.

ABSTRACT

Photocatalytic conversion of carbon dioxide (CO_2) to solar fuels is a promising solution to resolve the energy crisis and global warming issues. The overall efficiency of photoreduction of CO_2 to fuels can be improved through the development of highly efficient catalyst and suitable photoreactor configuration. Hence, the main objective of this research work was to design a photocatalytic reactor system and synthesize cobalt-aluminium-lanthanum-layered double hydroxide (CoAlLa-LDH) modified with graphitic carbon nitride (g-C_3N_4) and titanium carbon ($Ti_3C_2T_{A/R}$) MXene for enhanced photocatalytic reduction of CO_2 to renewable fuels. Initially, a novel CoAlLa-LDH was synthesized by co-precipitation method that has hexagonal nanosheet structure. The $Ti_3C_2T_{A/R}$ was synthesized through controlled etching with hydrogen fluoride acid that resulted in the formation of layered structured Ti_3C_2 MXene embedded with anatase and rutile phases of titanium dioxide (TiO_2). The $Ti_3C_2T_{A/R}$ having layered structure and embedded TiO_2 effectively acted as electrons reservoir and electrons mediator, respectively. Graphitic carbon nitride (g-C_3N_4) nanosheets were obtained through thermal heating and subsequent sonication. g-C_3N_4, CoAlLa-LDH and $Ti_3C_2T_{A/R}$ were hybridized to obtain g-C_3N_4/CoAlLa-LDH, g-C_3N_4/$Ti_3C_2T_{A/R}$, $Ti_3C_2T_{A/R}$/CoAlLa-LDH and g-C_3N_4/$Ti_3C_2T_{A/R}$/CoAlLa-LDH composites with layer-by-layer assemblies. The performance of photocatalysts was investigated through photocatalytic reduction of CO_2 with water (H_2O), dryreforming (DRM) and bireforming (BRM). Among LDHs the $Co_2Al_{0.95}La_{0.05}$-LDH showed maximum photocatalytic reduction of CO_2 with H_2O resulting in production rate of 21.80 and 25.5 μmolegcat^{-1}h^{-1} for CO and CH_4, respectively. The g-C_3N_4/$Ti_3C_2T_{A/R}$/$Co_2Al_{0.95}La_{0.05}$-LDH sample resulted in maximum CO and CH_4 production rate of 106 and 49.8 μmole gcat^{-1}h^{-1} through photocatalytic reduction of CO_2 with H_2O. The g-C_3N_4/$Ti_3C_2T_{A/R}$ sample showed very good performance in photocatalytic DRM with production of 73.31 and 51.24 μmole gcat^{-1}h^{-1} for CO and H_2, respectively. The g-C_3N_4/$Ti_3C_2T_{A/R}$/$Co_2Al_{0.95}La_{0.05}$-LDH sample, through photocatalytic BRM showed maximum CO and H_2 production of 47.81 and 73.31 μmole gcat^{-1}h^{-1} with higher selectivity towards H_2 production that is a high-quality syngas. The best performing g-C_3N_4/$Ti_3C_2T_{A/R}$/$Co_2Al_{0.95}La_{0.05}$-LDH catalyst in the fixed bed photoreactor for photocatalytic BRM was compared with multistage mesh photoreactor (MSM). The MSM showed syngas production of 1.81 and 1.22 folds higher as compared to fixed bed photoreactor for CO and H_2 respectively. The effects of various parameters such as amount of catalyst, feed ratio and illumination time for the photocatalytic reduction of CO_2 was studied to optimize yield and selectivity of fuel products through response surface methodology. It was found that the optimum CO production was obtained at 0.143 g, 4.48 h and 1.67 while the optimum H_2 production obtained was at 0.143 g, 4.93 h, 1.41 of catalyst loading, time and feed ratio, respectively. Finally, Langmuir-Hinshelwood model was developed to investigate adsorption behaviours and photocatalytic oxidation and reduction process, fitted well with the experimental data. It was determined that CO and H_2 production were dependent on quantity of CO_2 and CH_4 in the feed, respectively. In conclusion the $Ti_3C_2T_{A/R}$ and g-C_3N_4 modified CoAlLa-LDH catalyst can produce high quality renewable syngas fuel with high selectivity towards H_2 production.

ABSTRAK

Fotomangkin penukaran karbon dioksida (CO_2) kepada bahan api suria merupakan penyelesaian yang berpotensi untuk menyelesaikan krisis tenaga dan isu pemanasan global. Kecekapan keseluruhan fotopenurunan CO_2 kepada bahan api dapat ditambah baik melalui pembangunan mangkin yang sangat cekap dan konfigurasi fotoreaktor yang sesuai. Oleh itu, objektif utama penyelidikan ini adalah untuk mereka bentuk sistem reaktor fotomangkin dan mensintesis dwihidroksida berlapis kobalt-aluminium-lantanum (CoAlLa-LDH) diubah suai dengan nitridia karbon bergrafit (g-C_3N_4) dan MXene karbon titanium ($Ti_3C_2T_{A/R}$) untuk penurunan fotomangkin CO_2 yang dipertingkatkan kepada bahan api boleh diperbaharui. Pada awalnya, CoAlLa-LDH novel disintesis melalui kaedah ko-pemendakan yang mempunyai struktur nanolembaran heksagon. $Ti_3C_2T_{A/R}$ disintesis melalui punaran terkawal dengan asid hidrogen florida yang menghasilkan pembentukan struktur berlapis Ti_3C_2 MXene terbenam dengan fasa anatase dan rutil titanium dioksida (TiO_2). $Ti_3C_2T_{A/R}$ yang mempunyai struktur berlapis dan TiO_2 terbenam ini masing-masing bertindak dengan berkesan sebagai takungan elektron dan pengantara elektron. Nanolembaran karbon nitrida bergrafit (g-C_3N_4) diperoleh melalui pemanasan terma dan sonikasi berikutnya. g-C_3N_4, CoAlLa-LDH dan $Ti_3C_2T_{A/R}$ dihibridkan untuk mendapatkan komposit g-C_3N_4/CoAlLa-LDH, g-C_3N_4/$Ti_3C_2T_{A/R}$, $Ti_3C_2T_{A/R}$/CoAlLa-LDH dan g-C_3N_4/$Ti_3C_2T_{A/R}$/CoAlLa-LDH dengan gabungan lapisan demi lapisan. Prestasi fotomangkin disiasat melalui penurunan fotomangkin CO_2 dengan air (H_2O), pembentukan semula kering metana (DRM) dan dwipembentukan semula metana (BRM). $Co_2Al_{0.95}La_{0.05}$-LDH menunjukkan penurunan fotomangkin CO_2 dengan H_2 yang maksimum berbanding LDH lain dengan kadar penghasilan CO dan CH_4 masing-masing 21.80 and 25.5 μmol $g_{cat}^{-1}h^{-1}$. Sampel g-C_3N_4/$Ti_3C_2T_{A/R}$/$Co_2Al_{0.95}La_{0.05}$-LDH memberikan keputusan kadar pengeluaran maksimum CO dan CH_4 masing-masing sebanyak 106 and 49.8 μmol $g_{cat}^{-1}h^{-1}$ melalui penurunan fotomangkin CO_2 dengan H_2O. Sampel g-C_3N_4/$Ti_3C_2T_{A/R}$ menunjukkan prestasi yang sangat baik dalam DRM fotomangkin dengan pengeluaran CO dan H_2 masing-masing sebanyak 73.31 dan 51.24 μmol $g_{cat}^{-1}h^{-1}$. Bagi sampel g-C_3N_4/$Ti_3C_2T_{A/R}$/$Co_2Al_{0.95}La_{0.05}$-LDH pula, BRM fotomangkin menunjukkan pengeluaran maksimum CO dan H_2 masing-masing sebanyak 47.81 dan 73.31 μmol $g_{cat}^{-1}h^{-1}$ dengan kememilihan lebih tinggi kepada pengeluaran H_2 yang merupakan singas berkualiti tinggi. Mangkin g-C_3N_4/$Ti_3C_2T_{A/R}$/$Co_2Al_{0.95}La_{0.05}$-LDH berprestasi terbaik dalam fotoreaktor lapisan tetap untuk BRM fotomangkin dibandingkan dengan fotoreaktor jejaring berbilang tahap (MSM). MSM menunjukkan pengeluaran singas CO dan H_2 masing-masing sebanyak 1.81 dan 1.22 kali ganda lebih tinggi berbanding fotoreaktor lapisan tetap. Kesan daripada pelbagai parameter seperti jumlah mangkin, nisbah suapan dan masa pencahayaan untuk penurunan fotomangkin CO_2 telah dikaji untuk mengoptimumkan hasil dan kememilihan produk bahan api melalui kaedah gerak balas permukaan. Didapati bahawa pengeluaran CO optimum diperoleh pada 0.143 g, 4.48 j dan 1.41 manakala pengeluaran H_2 optimum diperoleh pada 0.143 g, 4.93 j, 1.41 masing-masing bagi pemuatan mangkin, masa dan nisbah suapan. Akhir sekali, model Langmuir-Hinshelwood yang dibangunkan untuk mengkaji kelakuan penjerapan dan proses pengoksidaan dan penurunan fotomangkin, sangat bertepatan dengan data eksperimen. Ditentukan bahawa pengeluaran CO dan H_2 masing-masing bersandar pada kuantiti CO_2 dan CH_4 dalam suapan. Kesimpulannya, mangkin CoAlLa-LDH diubah suai $Ti_3C_2T_{A/R}$ dan g-C_3N_4 dapat menghasilkan bahan api singas boleh diperbaharui berkualiti tinggi dengan kememilihan tinggi untuk pengeluaran H_2.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

AQY	-	Apparent quantum yield
BET	-	Braunauer-Emmer-Teller
BRM	-	Bireforming of methane
CB	-	Conduction band
CBM	-	Conduction band minimum
CO_2	-	Carbon dioxide
EDS/EDX	-	Energy-dispersive X-ray spectroscopy
FESEM	-	Field Emission Scanning Electron Microscope
FID	-	Flame Ionization Detector
F-T	-	Fischer-Tropsch
FTIR	-	Fourier-transform infrared spectroscopy
GHG	-	Greenhouse gas
GO	-	Graphene oxide
HRTEM	-	High Resolution Transmission Electron Microscopy
L-H	-	Langmuir-Hinshelwood
LDH	-	Layered double hydroxide
OCN	-	Oxygen doped graphitic carbon nitride
pCN	-	Protonated carbon nitride
PL	-	Photoluminescence
QY	-	Quantum yield
RGO	-	Reduced Graphene Oxide
RSM	-	Response surface methodology
SRM	-	Steam reforming of methane
UV/Vis	-	Ultraviolet Visible
XPS	-	X-ray Photoelectron spectroscopy
XRD	-	X-ray Diffraction
1D	-	One dimensional
2D	-	Two dimensional
3D	-	Three dimensional

LIST OF SYMBOLS

α	-	Absorption coefficient
E	-	Activation energy
β	-	Full width at half maximum
n	-	Concentration of electrons
p	-	Concentration of holes
N_c	-	Effective density state of CBM
N_v	-	Effective density state of VBM
e^-	-	Electron
E_p	-	Energy of photon
Eg	-	Energy bandgap
H	-	Heat of reaction
h_+	-	Hole
KJ	-	Kilo Joule
L	-	Length
I	-	Light intensity (mW/cm^2)
μm	-	Micrometre
P	-	Pressure
d		Plan spacing scattering angle
h	-	Planks constant
f	-	Photon flux
I_p	-	Photon Irradiance
k_B		Boltzmann constant
T	-	Temperature
θ	-	Angle of incident beam
W	-	Watt
λ	-	Wavelength

LIST OF APPENDICES

CHAPTER 1

INTRODUCTION

1.1 Research Background

Energy is vital for obtaining primary needs as well as for maintaining secure and improved living standards. This excessive energy usage is causing high use of fossil fuels, leading to energy dearth and production of CO_2. Moreover, CO_2 is one of the major greenhouse gases which results in global warming, a major environmental concern [1, 2]. Different approaches have been employed to mitigate CO_2 effects, in particular, reduction of CO_2 emission at the source, CO_2 capture and storage; and reutilization of CO_2 by conversion to value added chemicals. Among all, CO_2 utilization for the production of renewable fuels is the more attractive pathway, thereby relieving our dependency on traditional fossil fuels. However, these technologies have disadvantages that include: high electrical voltage and high temperature requirements to break the stable CO_2 molecule, limitations of raw materials, high cost of operation, and unsustainability [3]. Therefore, the employment of conversion of CO_2 to fuels through photocatalysis would be effective alternative to other processes [4].

The photocatalytic CO_2 reduction can be obtained through various reductants to obtain the desired fuel products. Through photocatalytic CO_2 reduction with water (H_2O) results in formation of methane (CH_4) and carbon monoxide (CO). The photocatalytic dry reforming (DRM) is conducted in the presence methane as reductant for the formation of syngas that is the combination of CO and hydrogen (H_2). The photocatalytic bireforming of methane (BRM) is conducted in the existence of H_2O and CH_4 resulting in the formation of syngas (CO, H_2) that has appeared as prospective energy source in several petrochemical industries to generate synthetic fuels through Fischer–Tropsch process [5].

Usually, the DRM and BRM processes are conducted at elevated temperature and demand high input energy, thus making the process uneconomical. In this scenario, photocatalytic DRM and BRM provides a cleaner technology by utilizing only light irradiation, while the process occurs at room temperature and atmospheric pressure.

The sunlight energy is acquired and collected in molecular bonds, similar to the natural photosynthesis process [6]. Photocatalysis over semiconductors is activated by the light of energy absorption, larger than their band gap, resulting in origination of excited electron (e^-) and a positive hole (h^+) pair that subsequently reduce and oxidize CO_2 and reductant, respectively. In photocatalysis, the excitation of electrons occur when light falls on the surface of photocatalyst which leads to the conversion of CO_2 to fuel [7]. The CO_2 conversion by phototechnology would satisfy the energy challenges and solve the environmental problems [8]. However, the efficiency of photocatalytic activity and selectivity is lower for CO_2 photoreduction that is needed to be improved. The performance of photocatalytic process can be improved by the use of novel photocatalyst in the efficient photoreactors [9].

Although, substantial development in the strategies to enhance the efficiency of semiconductor materials has been accomplished, however, the practical applications of these photocatalyst for CO_2 reduction have still limited conversion efficiency due to low utilization of light and fast charge carrier recombination. To make CO_2 conversion technique practically economic and industrial scalable, research should aim on increasing the overall CO_2 photoconversion efficiency and selectivity [10]. Hence, for the conversion of CO_2 into valuable chemicals such as CO, CH_3OH, CH_4, HCOOH and HCHO numerous semiconductors such as TiO_2 [11], ZnO [12], WO_3 [13] , SnO_2, CdS, α-Fe_2O_3 [14], Cu_2O [15, 16], and SiC [17] have been implemented to fabricate profecient photocatalytic systems for CO_2 photo-reduction to hydrocarbon fuels. However, the practical applications of these photocatalyst for CO_2 reduction are still limited by the efficiency due to less utilization of light and quick charge carrier recombination.

In this scenario, graphitic carbon nitride (g-C_3N_4), a visible light active semiconductor material, has attracted considerable interest because of the distinct layered structure, excellent thermal and chemical stabilities, low expense and simple synthesis. However, the photocatalytic activity of pristine g-C_3N_4 for CO_2 reduction is still very low due to rapid charge recombination. For this purpose, the photocatalytic CO_2 reduction efficiency improvement is obtained through coupling g-C_3N_4 with a second semiconductor, cocatalyst and/or photosensitizers to fabricate a multi-component composite photocatalyst with enhanced photocatalytic performance.

In the quest for materials having photocatalytic properties, high adsorption capacity and alkaline nature, the Layered Double Hydroxide (LDH) is getting attention as a potential photocatalyst due to its high adsorption capacity, high surface area, and semiconductor properties [18]. Moreover, the alkaline nature of LDH helps to adsorb the acidic CO_2. LDHs, with the general stoichiometry $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2]^{x+}(An)_{x/n}\bullet mH_2O$, are a class of 2D layered materials encompassing positively charged edge-sharing MO_6 octahedra layers with charge compensating anions between the interlayers [19]. In this regard, the earth-abundant Zn, Ni and Co based LDH catalysts have drawn consideration as photocatalysts for CO_2 reduction [20].

Among the LDHs, CoAl-LDH has found widespread application for photoreduction of CO_2 due to its strong performance and stability [21]. However, pristine LDHs usually display weak quantum efficiency under light irradiation because of sluggish charge carrier movement and high electron–hole recombination. Approaches to enhance LDH performance include research on ternary LDHs with the modification or doping of cations has reflected the properties of added cation that resulted in the improvement in photocatalytic activity. Doping of semiconductors results in: (i) modification of the structure surface, (ii) improved spectral response, (iii) variation in the bandgap, (iv) reduction in the electron–holes recombination and (v) formation of crystalline defects, resulting in improvement in photocatalytic activity [22, 23].

In this scenario, Ahmad et al [24] found that the incorporation of third metal Cu to the ZnGa-LDH improved the photocatalytic activity. Similarly, Parida et al [25] studied the influence on textural properties and photoactivity of Mg/Al+Fe-LDH by varying the atomic ratios of Al^{3+}/Fe^{3+}. Parida et al [26] further extended the work to study the effect of Co divalent cation Cu+Co/Cr LDH by altering the atomic ratio of (Cu^{2+}/Co^{2+}) to observe the effect of Co^{2+} on electronic and structural properties for photocatalytic activity of Cu/Cr LDHs. The combined effect of binary cations, enhanced charge carrier capability of cobalt and even pores dissemination led to enhanced photocatalytic activity.

LDHs are all exciting materials with attractive properties but their applications are still limited due to their inherent shortages [27]. Therefore, a series of strategies have been adopted to couple LDH materials with other materials to improve the CO_2 photocatalytic reduction efficiency. For example, compounding with other conductive substances such as Pt/ZnCr LDH [28], Ag/Zn_3Ga-LDH [29], Ru/MgAl-LDH [30], rGO/NiTi-LDH [31], and CoAl-LDHs/RGO [32] have been utilized to improve the photocatalytic activity of LDHs. Nevertheless, the efficiency of these materials is still low to curb large-scale application. Another strategy is combining LDH with other semiconductors is one of the most efficient tactics to improve the photogenerated charge carriers separation efficiency during the photocatalytic process. For instance, the coupling of g-C_3N_4 and NiAl-LDH resulted in the formation of 2D/2D interface heterostructures that showed the production of CO and H_2. However, the selectivity towards H_2 production was very low resulting in production of a low-quality syngas [33]. Similarly, urchin-like g-C_3N_4/NiAl-LDH heterojunction was constructed for excellent CO production, however, the study on the production of other fuels such as CH_4 and H_2 were not conducted. Therefore, the coupling of LDH material with a cocatalyst having highly active sites is one of the most effective approach to enhance the performance of LDHs for CO_2 reduction to selective fuels such as H_2 and CH_4 is very important [34].

Titanium Carbide (Ti_3C_2) a typical MXene has been enormously studied as a cheap cocatalyst due to their outstanding electrical conductivity, elemental composition adjustability, even layered structure and controllable surface functional

groups. Ti_3C_2 possesses 2D structure and therefore has the possibility to form intimate 2D/2D interface with other 2D materials. The resultant photocatalyst form the intimate connection that can greatly enhance the photo-induced electron-hole pairs separation. For example, Cao et al. [35] hybridized ultrathin Ti_3C_2 with Bi_2WO_6 nanosheets to form a 2D/2D Ti_3C_2/Bi_2WO_6 heterojunction, resulting in the substantially improved photocatalytic CO_2 reduction in comparison to pristine Bi_2WO_6 nanosheets. The Ti_3C_2 has also been coupled with g-C_3N_4 that has resulted in enhanced photocatalytic activity towards CO_2 reduction. For example, Yang et al. [22] also formed 2D/2D Ti_3C_2/g-C_3N_4 ultrathin heterojunction that increased photocatalytic H_2O_2 production activity, attributed to the outstanding electronic conductivity of Ti_3C_2 for boosting spatial charge carrier separation. Similarly, Ti_3C_2 was combined with a photocatalytic material (BiOBr) that demonstrated superb photocatalytic activities in H_2O detoxification and splitting [20]. The coupling of Ti_3C_2 has also been done successfully to enhance the photocatalytic reduction of CO_2. For instance, Co-Co layered double hydroxide has been coupled with $Ti_3C_2T_X$ nanosheets (Co-Co LDH/TNS) to integrate the functional and structural merits of active Co species with conductive $Ti_3C_2T_X$ nanosheets for the formation of hierarchical nanoarray architecture composed of ultrathin nanosheets, which promoted the separation of photogenerated charge carriers and accelerated electrons transmission. Yang et al [18] fabricated urchin-like CoZnAl-LDH/RGO/g-C_3N_4 heterojunction that formed Z-Scheme heterojunction resulting in the restriction of the recombination of photoinduced electron-hole pairs that caused the enhancement of the oxidizability and reducibility of CoZnAl-LDH and g-C_3N_4. Z-scheme photocatalysts are named as due to their charge transfer mechanism similarity to natural photosynthesis, in which the charge-carrier transportation pathway follow a two-step photoexcitation that resembles the English letter “Z”. Although distinct works have been done on Ti_3C_2 coupling with g-C_3N_4 or LDH, however, further research is required to study the effect of binary and ternary composite to generate photocatalysts with excellent photocatalytic properties towards CO_2 reduction.

After exploring the photocatalytic system process optimization is important to identify the optimum reaction conditions such as catalyst loading, time and feed ratio towards in achieving the maximum fuel production is necessary. To understand the interaction between input process parameters and output responses such as feed conversion and product yield is necessary. Therefore, the surface response surface

methodology (RSM) has been used for experimental design, optimize and investigate the effect on conversion of reactant and products yield. Through this technique Delavari et al [36] was able to achieve maximum find the optimized conversion of CO and CH_4 up to 37.9% and 48.7%, respectively**.** Umar et al [37] optimized H_2 production by employing RSM technique. Therefore, RSM can be a useful technique to optimize the photocatalytic reaction process conditions. understand the kinetics of a photocatalytic reaction is important in order to determine the rate determining step and the right pathway. Delavari et al [36] employed Langmuir–Hinshelwood model to find yield rates of products reliant on effective reactants adsorption and products desorption on the catalyst surface.

Tahir et al [38] was able to modulate the reaction of CO_2 and H_2O vapours over the larger mesoporous In-doped TiO_2 catalyst surface area. Therefore, the L-H model can be helpful to modulate the photocatalytic CO_2 reduction to study the effect of rate constants on the photocatalytic activity.

In this study, $Ti_3C_2T_{A/R}$ MXene and g-C_3N_4 modified CoAlLa-LDH structure composite is synthesized and test for photocatalytic activity through CO_2 reduction with H_2O, DRM and BRM. The Z-scheme formation between $Ti_3C_2T_{A/R}$ MXene and g-C_3N_4 modified CoAlLa-LDH possessing the merits of conductive and semiconductive components can exhibits photocatalytic activity. The best performing catalyst is used to compare the result between fixed bed reactor and Multistage mesh photoreactor (MSM). The effects of various parameters such as amount of catalyst, feedstock gases ratio and illumination time for the photocatalytic reduction of CO_2 was studied to optimize yield and selectivity of fuel products through response surface methodology (RSM). The Langmuir-Hinshelwood model is used to study the adsorption behaviours and photocatalytic oxidation and reduction process.

1.2 Problem Statement and Hypothesis

The fossil fuels exhaustion and the devastating environmental pollution arising from their combustion have been known as two key challenges in the future. With the diminution of fossil-fuel reserves and emission of greenhouse gas CO_2, an important challenge faced by human beings is to search a clean and sustainable alternate-energy sources. Instead of CO_2 sequestration, CO_2 can be captured and reused as a carbon source for the production of other valuable chemicals. However, breaking stable CO_2 molecule requires higher energy input, making this process costly. Different approaches have been used to mitigate CO_2 effects, in particular, reduction of CO_2 emission at the source, CO_2 capture and storage; and reutilization of CO_2 by conversion to value added chemicals. Among these approaches, CO_2 utilization for the production of valuables fuels and chemicals is the more attractive approach for production of renewable fuels. The reutilization of CO_2 to fuels can be obtained through: chemical conversions, electrochemical reductions, biological conversions, reforming and photochemical reductions [39]. Many photocatalysts are in use but yet lower CO_2 conversion, lesser yield rates and selectivity were observed [11].

Among them, g-C_3N_4, a visible light-responsive semiconductor material, has drawn substantial interest due to the distinct layered structure, excellent chemical and thermal stabilities, low cost and simple synthesis. However, the photocatalytic activity of pure g-C_3N_4 for CO_2 reduction is still very low and mainly limited owing to the rapid charge recombination. The as-prepared g-C_3N_4 usually has high recombination rate of electrons and holes in bulk g-C_3N_4, which highly impact the photocatalytic activity. In this regard, several approaches have been thus adopted to improve photocatalytic CO_2 reduction activity of g-C_3N_4 photocatalysts [40]. The coupling of g-C_3N_4 with other semiconductors having appropriate band edge positions and high sorption capacity have been adopted to further promote the photocatalytic efficiency. However, the improvements were very little that caused various disadvantages, for example, shielding of irradiations, trapping of charges produced, using redox active sites, unselective adsorption of reactants and products, *etc*.[41]. This urges to find new and highly efficient composite photocatalyst for photocatalytic reduction of CO_2 to duels under UV and visible light irradiations.

Moreover, the fabrication of a novel photoreactor that serve larger exposed surface area to the light irradiations is needed so that photons can effectively and constantly be distributed throughout the entire photocatalyst surface. To this point, the challenges and possible solution strategies are:

1. Many semiconductors have been used as photocatalysts for CO_2 reduction, however the developed photocatalysts have weak light harvesting in visible light region and pose problem of fast charge carrier recombination. Among semiconductor materials, g-C_3N_4 is widely investigated because of abundant availability, comparatively cheap and numerous other advantageous. Also, the exploration of novel LDH photocatalyst by fine tuning the structural, compositional, band-gap and surface reaction sites promote light harvesting and retarding the charge recombination for practical application as a photocatalyst for the conversion of CO_2 to fuel.

2. The incorporation of Co-based LDHs catalyst that respond to visible light photocatalytic performance, have better surface charge transfer and low recombination of electron−hole would show high photocatalytic activity towards CO_2 photoreduction. The addition of electrons rich lanthanum (La) to the CoAlLa-LDH would enhance the photocatalytic activity by enhancing the reductive sites to increase the separation of photogenerated charges due to the formation of vacancy rich ternary CoAlLa-LDH. The presence aluminum in the LDHs have shown high selectivity towards CO_2 reduction and the Co^{2+} electron transfer to the Al^{3+} electrodeficient cation produce a delay in the rate of the electron–hole pair recombination. Furthermore, the presence of Al^{3+} imposes superior crystallinity to the LDH.

3. The Ti_3C_2 MXene with a large work function, good structural stability, and excellent visible light harvesting ability is electronically and catalytically considered as a suitable CO_2 reduction cocatalyst that can promote the migration and separation of photo-induced charge carriers because of its strong electronic conductivity. The Ti_3C_2 through controlled treatment could be converted $Ti_3C_2T_{A/R}$ with enhanced photocatalytic properties due to the formation of TiO_2.

4. A photostable photocatalyst is highly needed that has high light absorption and utilization efficiency, superior charge separation, impedes recombination, absorbs in visible region and has a larger reactive surface area to adsorb hogh amount of CO_2. Nevertheless, by coupling of g-C_3N_4, tri metallic CoAlLa-LDH and Ti_3C_2 materials would result in the formation of a composite with high photocatalytic activity that is ascribed to the strong interfacial interaction with formation of Z-scheme and electron rich linkers of oxygen defective La/Ti sites for superior charge-transfer separation. The CoAlLa-LDH and g-C_3N_4 would form a Z-scheme mechanism for electrons transfer whereas the $Ti_3C_2T_{A/R}$ with the presence of TiO_2 and Ti_3C_2 act as electrons mediator and electrons reservoir respectively. The substantially improved photocatalytic CO_2 reduction would be enhanced further due to the synergistic effect of electron rich lanthanum doped CoAlLa-LDH coupling with negatively charged highly conductive $Ti_3C_2T_{A/R}$ and semiconducting g-C_3N_4 leading to improved charge separation.

5. Maximum utilization of photons has always been a problem of concern in the photoreactors therefore, the fabrication of photocatalysts on mesh may provide large illuminated surface area to reactor volume ratio and efficient light and catalyst utilization/distribution. Hence, growing of CoAlLa-LDH, g-C_3N_4 and $Ti_3C_2T_{A/R}$ in multistage mesh (MSM) photoreactor to develop photocatalytic system is envisaged to success for the enhancement of the photoreduction of CO_2 to fuels.

6. The optimization of operating parameters would further be fruitful to maximize syngas (CO and H_2) production and selectivity. This would also be helpful to optimize operating the catalyst loading, reaction time and feed ratio. The Langmuir–Hinshelwood model developed to study the effect on dependent on desorption of the reactants surface reaction and desorption of products over the catalyst surface.

1.3 Research Objectives

The main objective of the research work is to increase the efficiency of photocatalytic reduction of CO_2 to fuels through fabricating efficient photocatalytic system. The objectives of this work include:

1. To synthesize and characterize $Ti_3C_2T_{A/R}$ and g-C_3N_4 modified CoAlLa-LDH composites for reduction of CO_2 under light irradaiations;
2. To investigate the photocatalytic performance of synthesized photocatalysts for CO_2 reductions to fuels using different reforming systems and photoreactors;
3. To conduct the optimization study of the parameters such as reaction time, effect of loading and feed ratio using response surface methodology;
4. To develop kinetic model for the determination of reaction rate parameters in photocatalytic reduction of CO_2 for the obtained heterojunction.

1.4 Scope of the Research

This research is aimed on solving some of the basic problems associated to low CO_2 photoreduction efficiency and selectivity towards fuel. In this viewpoint, synthesize and characterization of g-C_3N_4 and $Ti_3C_2T_{A/R}$ modified LDH photocatalysts were examined. The modification of LDH photocatalysts with g-C_3N_4 and $Ti_3C_2T_{A/R}$ were studied for photocatalytic reduction of CO_2 with H_2O. Some operating parameters effect such as mass of photocatalyst loading, feed ratios, and irradiation times were discussed. The effect of reductants such as H_2O and CH_4 and were studied on the production of fuels. The reaction mechanism of CO_2 reduction and quantum efficiency were studied and analyzed. The CO_2 conversion to fuels efficiency is associated to maximize yield rates of fuel products. The desired products obtained were CO and CH_4 when CO_2 was reduced in the presence of H_2O, while CO and H_2, a potential syngas when CO_2 was reduced in the presence of CH_4 through

photocatalytic dry reforming of methane (DRM) and in the presence of H_2O and CH_4 through photocatalytic bireforming of methane (BRM). Therefore, the detail on research scopes is as follows:

1. The photocatalyst such as g-C_3N_4, Ti_3C_2, $Ti_3C_2T_{A/R}$, CoAl-LDH, CoLa-LDH, CoAlLa-LDH, $Ti_3C_2T_{A/R}$/CoAlLa-LDH, g-C_3N_4/CoAlLa-LDH, g-C_3N_4/$Ti_3C_2T_{A/R}$/CoAlLa-LDH were synthesized. The LDHs were synthesized using coprecipitation, and subsequent hydrothermal treatment method. Ti_3C_2 and $Ti_3C_2T_{A/R}$ were obtained through controlled etching of Ti_3AlC_2. The prepared catalysts were characterized using some equipment analysis such as XRD, FESEM, FTIR, HRTEM, PL, RAMAN, XPS, and UV-Visible spectroscopy. The crystallinity, phase, morphology and structures, metals transition states and optical properties were determined through these characterizations.

2. The photoactivity of catalyst samples were conducted to evaluate the performance of the catalyst samples. The fixed bed photoreactor was utilized to test the yield of CO, CH_4 through photocatalytic reduction of CO_2 with H_2O while yield of CO and H_2 were tested for photocatalytic reduction of CO_2 with CH_4 and H_2O+CH_4 through photocatalytic DRM and BRM, respectively. The photocatalysts were spread in the bottom of fixed bed photoreactor. The light used was a 35W HID Xe lamp having 20 $mWcm^{-2}$ light intensity fitted with a concentrator. Multistage Mesh (MSM) photoreactor was employed to compare the performance with Fixed bed reactor through photocatalytic BRM with the efficient performing photocatalyst.

3. The optimization of process parameters was conducted by utilizing response surface methodology (RSM). The parameters selected for optimization were catalyst loading, reaction time and effect of feed ratio.

4. The kinetic model was developed using Langmuir Hinshelwood mechanism to determine rate of reaction. A model equation was derived to examine the effect of parameters on the photocatalytic reaction.

1.5 Significance of the Study

The photocatalytic reduction of CO_2 was conducted to obtain CO and CH_4 in the presence of H_2O. Photocatalytic DRM and BRM were conducted to obtain syngas ($CO+H_2$) in the presence of CH_4 and CH_4+H_2O respectively. The photocatalyst composite obtained showed very good performance. The numerous outcomes of the research are described below:

1. A highly active ternary CoAlLa-LDH was formed through La^{3+} incorporation resulting in improvement of photogenerated charge carrier separation.

2. A facile etching strategy was adopted to construct hierarchical $TiO_{2A/R}$ nucleates on Ti_3C_2 nanosheets that form $Ti_3C_2/TiO_{2A/R}$ ($Ti_3C_2T_{A/R}$), where nanoscale $TiO_{2A/R}$ were in-situ formed and uniformly imbedded to cover the edges of the Ti_3C_2.

3. Electrons rich CoAlLa-LDH hybridization with $TiO_{2A/R}$ embedded Ti_3C_2 MXene and g-C_3N_4 through electrostatic assembly strategy resulting in formation of 2D/2D/2D hierarchical architecture with enhanced photocatalytic activity.

4. A new study for investigation of effect of photocatalytic CO_2 reduction with CH_4 and CO_2+CH_4 through photocatalytic DRM and BRM techniques respectively.

5. The effect of employment of MSM photoreactor on the photocatalytic through the increase of surface area and light irradiation utilization.

1.6 Outline of Thesis

This thesis is comprised of 7 chapters excluding all introductory pages, table of content and abstract. Chapter 1 consists of the introductory statements, problem statement, hypothesis, objectives, scope, study significance and outline of thesis. The literature survey on basics of photocatalysis and CO_2 reduction basics understanding

of photoreduction of CO_2, literature on Layered double hydroxides (LDH) and Ti_3C_2 MXene, literature on photoreactors, characterization techniques, development of kinetic models and Response surface methodology (RSM) were deliberated in Chapter 2.

In Chapter 3 a comprehensive explanation of the research methodology and order of the research, details of synthesize methods for the catalysts and carry out the photocatalytic experiments are provided. The equipment's employed for characterizations and the type of reactors employed for reduction of CO_2. The results obtained from the analysis of characterization are discussed in Chapter 4. The photocatalytic activity test though reduction with CO_2 with H_2O, DRM and BRM are discussed for different catalysts are conducted in chapter 5. Response surface methodology (RSM) employed for the optimization of parameters and L-H model developed for the photocatalytic process and are discussed in Chapter 6. Chapter 7 concludes the thesis with conclusions obtained from the research work and suggested recommendations for further research.

REFERENCES

1. Sun Z, Talreja N, Tao H, Texter J, Muhler M, Strunk J, et al. Catalysis of Carbon Dioxide Photoreduction on Nanosheets: Fundamentals and Challenges. Angewandte Chemie International Edition. 2018;57(26):7610-27.
2. Shen M, Zhang L, Shi J. Converting CO_2 into fuels by graphitic carbon nitride-based photocatalysts. Nanotechnology. 2018;29(41):412001.
3. Nguyen V-H, Wu JC. Recent developments in the design of photoreactors for solar energy conversion from water splitting and CO_2 reduction. Applied Catalysis A: General. 2018;550:122-41.
4. Shehzad N, Johari K, Murugesan T, Tahir M. Graphene Oxide as An Efficient Photocatalyst For Photocatalytic Reduction of CO_2 Into Solar Fuel. International Journal of Automotive & Mechanical Engineering. 2018;15(1).
5. Stroud T, Smith T, Le Saché E, Santos J, Centeno M, Arellano-Garcia H, et al. Chemical CO_2 recycling via dry and bi reforming of methane using Ni-Sn/Al_2O_3 and Ni-Sn/CeO_2-Al_2O_3 catalysts. Applied Catalysis B: Environmental. 2018;224:125-35.
6. Tahir B, Tahir M, Amin NAS. Tailoring performance of La-modified TiO_2 nanocatalyst for continuous photocatalytic CO_2 reforming of CH_4 to fuels in the presence of H_2O. Energy Conversion and Management. 2018;159:284-98.
7. Tahir M. Photocatalytic carbon dioxide reduction to fuels in continuous flow monolith photoreactor using montmorillonite dispersed Fe/TiO_2 nanocatalyst. Journal of Cleaner Production. 2018;170:242-50.
8. Ran J, Jaroniec M, Qiao SZ. Cocatalysts in Semiconductor-based Photocatalytic CO_2 Reduction: Achievements, Challenges, and Opportunities. Advanced materials. 2018;30(7):1704649.
9. Tahir M, Amin NAS. Photo-induced CO_2 reduction by hydrogen for selective CO evolution in a dynamic monolith photoreactor loaded with Ag-modified TiO_2 nanocatalyst. International Journal of Hydrogen Energy. 2017;42(23):15507-22.

10. Zhang D, Du X, Shi L, Gao R. Shape-controlled synthesis and catalytic application of ceria nanomaterials. Dalton Transactions. 2012;41(48):14455-75.
11. Nikokavoura A, Trapalis C. Alternative photocatalysts to TiO_2 for the photocatalytic reduction of CO_2. Applied Surface Science. 2017;391:149-74.
12. Iqbal M, Wang Y, Hu H, He M, Shah AH, Lin L, et al. Cu_2O-tipped ZnO nanorods with enhanced photoelectrochemical performance for CO_2 photoreduction. Applied Surface Science. 2018;443:209-16.
13. Lee J, Kim SK, Sohn Y. Understanding photocatalytic coupled-dye degradation and photoelectrocatalytic water splitting and CO_2 reduction over WO_3/MoO_3 hybrid nanostructures. Journal of Industrial and Engineering Chemistry. 2018.
14. Jiang Z, Wan W, Li H, Yuan S, Zhao H, Wong PK. A Hierarchical Z-Scheme alpha-Fe_2O_3/g-C_3N_4 Hybrid for Enhanced Photocatalytic CO_2 Reduction. Advanced materials. 2018;30(10).
15. Wang J-C, Zhang L, Fang W-X, Ren J, Li Y-Y, Yao H-C, et al. Enhanced photoreduction CO_2 activity over direct Z-scheme α-Fe_2O_3/Cu_2O heterostructures under visible light irradiation. ACS applied materials & interfaces. 2015;7(16):8631-9.
16. Kim C, Cho KM, Al-Saggaf A, Gereige I, Jung H-T. Z-scheme Photocatalytic CO_2 Conversion on Three-Dimensional $BiVO_4$/Carbon-Coated Cu_2O Nanowire Arrays under Visible Light. ACS Catalysis. 2018;8(5):4170-7.
17. Poudyal S, Laursen S. Insights into Elevated-Temperature Photocatalytic Reduction of CO_2 by H_2O. The Journal of Physical Chemistry C. 2018;122(15):8045-57.
18. Yang Y, Wu J, Xiao T, Tang Z, Shen J, Li H, et al. Urchin-like hierarchical CoZnAl-LDH/RGO/g-C_3N_4 hybrid as a Z-scheme photocatalyst for efficient and selective CO_2 reduction. Applied Catalysis B: Environmental. 2019;255:117771.
19. Wen Y, Rufford TE, Chen X, Li N, Lyu M, Dai L, et al. Nitrogen-doped $Ti_3C_2T_x$ MXene electrodes for high-performance supercapacitors. Nano Energy. 2017;38:368-76.

20. Chen W, Han B, Xie Y, Liang S, Deng H, Lin Z. Ultrathin Co-Co LDHs nanosheets assembled vertically on MXene: 3D nanoarrays for boosted visible-light-driven CO_2 reduction. Chemical Engineering Journal. 2020;391:123519.
21. Xu H, Wang B, Shan C, Xi P, Liu W, Tang Y. Ce-doped NiFe-layered double hydroxide ultrathin nanosheets/nanocarbon hierarchical nanocomposite as an efficient oxygen evolution catalyst. ACS Applied Materials & Interfaces. 2018;10(7):6336-45.
22. Miao Y-f, Guo R-t, Gu J-w, Liu Y-z, Wu G-l, Duan C-p, et al. Fabrication of β-In_2S_3/NiAl-LDH heterojunction photocatalyst with enhanced separation of charge carriers for efficient CO_2 photocatalytic reduction. Applied Surface Science. 2020;527:146792.
23. Jo W-K, Moru S, Tonda S. A green approach to the fabrication of a TiO_2/NiAl-LDH core–shell hybrid photocatalyst for efficient and selective solar-powered reduction of CO_2 into value-added fuels. Journal of Materials Chemistry A. 2020;8(16):8020-32.
24. Ahmed N, Morikawa M, Izumi Y. Photocatalytic conversion of carbon dioxide into methanol using optimized layered double hydroxide catalysts. Catalysis Today. 2012;185(1):263-9.
25. Parida K, Satpathy M, Mohapatra L. Incorporation of Fe^{3+} into Mg/Al layered double hydroxide framework: effects on textural properties and photocatalytic activity for H_2 generation. J Mater Chem. 2012;22(15):7350-7.
26. Parida K, Mohapatra L, Baliarsingh N. Effect of Co^{2+} substitution in the framework of carbonate intercalated Cu/Cr LDH on structural, electronic, optical, and photocatalytic properties. The Journal of Physical Chemistry C. 2012;116(42):22417-24.
27. Cao Y, Li G, Li X. Graphene/layered double hydroxide nanocomposite: Properties, synthesis, and applications. Chemical Engineering Journal. 2016;292:207-23.
28. Katsumata K-i, Sakai K, Ikeda K, Carja G, Matsushita N, Okada K. Preparation and photocatalytic reduction of CO_2 on noble metal (Pt, Pd, Au) loaded Zn–Cr layered double hydroxides. Materials Letters. 2013;107:138-40.
29. Kawamura S, Zhang H, Tamba M, Kojima T, Miyano M, Yoshida Y, et al. Efficient volcano-type dependence of photocatalytic CO_2 conversion into

methane using hydrogen at reaction pressures up to 0.80 MPa. Journal of Catalysis. 2017;345:39-52.

30. Ren J, Ouyang S, Xu H, Meng X, Wang T, Wang D, et al. Targeting Activation of CO_2 and H_2 over Ru-Loaded Ultrathin Layered Double Hydroxides to Achieve Efficient Photothermal CO_2 Methanation in Flow-Type System. Advanced Energy Materials. 2017;7(5).
31. Li B, Zhao Y, Zhang S, Gao W, Wei M. Visible-light-responsive photocatalysts toward water oxidation based on NiTi-layered double hydroxide/reduced graphene oxide composite materials. ACS Applied Materials & Interfaces. 2013;5(20):10233-9.
32. Kumaresan A, Yang S, Zhao K, Ahmad N, Zhou J, Zheng Z, et al. Facile development of CoAl-LDHs/RGO nanocomposites as photocatalysts for efficient hydrogen generation from water splitting under visible-light irradiation. Inorganic Chemistry Frontiers. 2019;6(7):1753-60.
33. Tonda S, Kumar S, Bhardwaj M, Yadav P, Ogale S. g-C_3N_4/NiAl-LDH 2D/2D Hybrid Heterojunction for High-Performance Photocatalytic Reduction of CO_2 into Renewable Fuels. ACS Applied Materials & Interfaces. 2018;10(3):2667-78.
34. Shi Q, Huang J, Yang Y, Wu J, Shen J, Liu X, et al. In-situ construction of urchin-like hierarchical g-C_3N_4/NiAl-LDH hybrid for efficient photoreduction of CO2. Materials Letters. 2020;268:127560.
35. Cao S, Shen B, Tong T, Fu J, Yu J. 2D/2D heterojunction of ultrathin MXene/Bi_2WO_6 nanosheets for improved photocatalytic CO_2 reduction. Advanced Functional Materials. 2018;28(21):1800136.
36. Delavari S, Amin NAS. Photocatalytic conversion of CO_2 and CH_4 over immobilized titania nanoparticles coated on mesh: Optimization and kinetic study. Applied Energy. 2016;162:1171-85.
37. Umer M, Tahir M, Usman Azam M, Tasleem S, Abbas T, Muhammad A. Synergistic effects of single/multi-walls carbon nanotubes in TiO_2 and process optimization using response surface methodology for photo-catalytic H_2 evolution. Journal of Environmental Chemical Engineering. 2019;7(5):103361.

38. Tahir M, Amin NS. Indium-doped TiO_2 nanoparticles for photocatalytic CO_2 reduction with H_2O vapors to CH_4. Applied Catalysis B: Environmental. 2015;162:98-109.
39. Braham R, Harris A. A complete multi-scale simulation of light absorption within a fluidized bed photoreactor using integrated particle, fluid and photon behaviour models. Physical Chemistry Chemical Physics. 2013;15(29):12373-85.
40. Dai K, Lu L, Liu Q, Zhu G, Wei X, Bai J, et al. Sonication assisted preparation of graphene oxide/graphitic-C_3N_4 nanosheet hybrid with reinforced photocurrent for photocatalyst applications. Dalton Transactions. 2014;43(17):6295-9.
41. Liu S, Chen F, Li S, Peng X, Xiong Y. Enhanced photocatalytic conversion of greenhouse gas CO_2 into solar fuels over g-C_3N_4 nanotubes with decorated transparent ZIF-8 nanoclusters. Applied Catalysis B: Environmental. 2017;211:1-10.
42. Barbir F, Veziroğlu T, Plass H. Environmental damage due to fossil fuels use. International Journal of Hydrogen Energy. 1990;15(10):739-49.
43. Albo J, Luis P, Irabien A. Carbon dioxide capture from flue gases using a cross-flow membrane contactor and the ionic liquid 1-ethyl-3-methylimidazolium ethylsulfate. Industrial & Engineering Chemistry Research. 2010;49(21):11045-51.
44. Bafaqeer A, Tahir M, Amin NAS. Well-designed 2D/2D ZnV_2O_6/g-C_3N_4 nanosheets heterojunction with faster charges separation via pCN as mediator towards enhanced photocatalytic reduction of CO_2 to fuels. Applied Catalysis B: Environmental. 2018.
45. Sakakura T, Choi J-C, Yasuda H. Transformation of carbon dioxide. Chemical Reviews. 2007;107(6):2365-87.
46. Das S, Daud WW. A review on advances in photocatalysts towards CO_2 conversion. RSC Advances. 2014;4(40):20856-93.
47. Dincer I. Renewable energy and sustainable development: a crucial review. Renewable and Sustainable Energy Reviews. 2000;4(2):157-75.
48. Nowotny J, Dodson J, Fiechter S, Gür TM, Kennedy B, Macyk W, et al. Towards global sustainability: Education on environmentally clean energy technologies. Renewable and Sustainable Energy Reviews. 2017.

49. Duraccio V, Gnoni MG, Elia V. Carbon capture and reuse in an industrial district: A technical and economic feasibility study. Journal of CO_2 Utilization. 2015;10:23-9.
50. Roy SC, Varghese OK, Paulose M, Grimes CA. Toward solar fuels: photocatalytic conversion of carbon dioxide to hydrocarbons. ACS Nano. 2010;4(3):1259-78.
51. Hepbasli A. A key review on exergetic analysis and assessment of renewable energy resources for a sustainable future. Renewable and Sustainable Energy Reviews. 2008;12(3):593-661.
52. Menanteau P, Finon D, Lamy M-L. Prices versus quantities: choosing policies for promoting the development of renewable energy. Energy Policy. 2003;31(8):799-812.
53. Bachu S. Screening and ranking of sedimentary basins for sequestration of CO_2 in geological media in response to climate change. Environmental Geology. 2003;44(3):277-89.
54. Cuéllar-Franca RM, Azapagic A. Carbon capture, storage and utilisation technologies: a critical analysis and comparison of their life cycle environmental impacts. Journal of CO_2 Utilization. 2015;9:82-102.
55. Kainiemi L, Eloneva S, Toikka A, Levänen J, Järvinen M. Opportunities and obstacles for CO_2 mineralization: CO_2 mineralization specific frames in the interviews of Finnish carbon capture and storage (CCS) experts. Journal of Cleaner Production. 2015;94:352-8.
56. Spigarelli BP, Kawatra SK. Opportunities and challenges in carbon dioxide capture. Journal of CO_2 Utilization. 2013;1:69-87.
57. Centi G, Perathoner S. Opportunities and prospects in the chemical recycling of carbon dioxide to fuels. Catalysis Today. 2009;148(3-4):191-205.
58. Saeidi S, Amin NAS, Rahimpour MR. Hydrogenation of CO_2 to value-added products—a review and potential future developments. Journal of CO_2 Utilization. 2014;5:66-81.
59. Frese KW, Leach S. Electrochemical reduction of carbon dioxide to methane, methanol, and CO on Ru electrodes. Journal of the Electrochemical Society. 1985;132(1):259-60.

60. Chen P, Min M, Chen Y, Wang L, Li Y, Chen Q, et al. Review of biological and engineering aspects of algae to fuels approach. International Journal of Agricultural and Biological Engineering. 2010;2(4):1-30.
61. Aresta M, Dibenedetto A, Angelini A. Catalysis for the valorization of exhaust carbon: from CO_2 to chemicals, materials, and fuels. Technological use of CO_2. Chemical Reviews. 2013;114(3):1709-42.
62. Joo O-S, Jung K-D, Moon I, Rozovskii AY, Lin GI, Han S-H, et al. Carbon dioxide hydrogenation to form methanol via a reverse-water-gas-shift reaction (the CAMERE process). Industrial & Engineering Chemistry Research. 1999;38(5):1808-12.
63. Ma J, Sun N, Zhang X, Zhao N, Xiao F, Wei W, et al. A short review of catalysis for CO_2 conversion. Catalysis Today. 2009;148(3):221-31.
64. Wang B, Li Y, Wu N, Lan CQ. CO_2 bio-mitigation using microalgae. Applied Microbiology and Biotechnology. 2008;79(5):707-18.
65. Bertau M, Offermanns H, Plass L, Schmidt F, Wernicke H-J. Methanol: The Basic Chemical and Energy Feedstock of the Future: Asinger's Vision Today: Springer Science & Business Media; 2014.
66. Yuan L, Xu Y-J. Photocatalytic conversion of CO_2 into value-added and renewable fuels. Applied Surface Science. 2015;342:154-67.
67. Hennig H, Billing R. Advantages and disadvantages of photocatalysis induced by light-sensitive coordination compounds. Coordination Chemistry Reviews. 1993;125(1-2):89-100.
68. Huff CA, Sanford MS. Cascade catalysis for the homogeneous hydrogenation of CO_2 to methanol. Journal of the American Chemical Society. 2011;133(45):18122-5.
69. Tahir M, Amin NS. Advances in visible light responsive titanium oxide-based photocatalysts for CO_2 conversion to hydrocarbon fuels. Energy Conversion and Management. 2013;76:194-214.
70. Evans DG, Slade RC. Structural aspects of layered double hydroxides. Layered double hydroxides: Springer; 2006. p. 1-87.
71. László B, Baán K, Varga E, Oszkó A, Erdőhelyi A, Kónya Z, et al. Photo-induced reactions in the CO2-methane system on titanate nanotubes modified with Au and Rh nanoparticles. Applied Catalysis B: Environmental. 2016;199:473-84.

72. Li X, Yu J, Low J, Fang Y, Xiao J, Chen X. Engineering heterogeneous semiconductors for solar water splitting. Journal of Materials Chemistry A. 2015;3(6):2485-534.
73. Hurum DC, Gray KA, Rajh T, Thurnauer MC. Recombination pathways in the Degussa P25 formulation of TiO_2: surface versus lattice mechanisms. The Journal of Physical Chemistry B. 2005;109(2):977-80.
74. Wen J, Xie J, Chen X, Li X. A review on g-C_3N_4 based photocatalysts. Applied Surface Science. 2017;391:72-123.
75. Kittel C. Introduction to solid state physics: Wiley; 2005.
76. Ohtani B. Revisiting the fundamental physical chemistry in heterogeneous photocatalysis: its thermodynamics and kinetics. Physical Chemistry Chemical Physics. 2014;16(5):1788-97.
77. Li K, Peng B, Peng T. Recent advances in heterogeneous photocatalytic CO_2 conversion to solar fuels. ACS Catalysis. 2016.
78. Brus LE. Electron–electron and electron-hole interactions in small semiconductor crystallites: The size dependence of the lowest excited electronic state. The Journal of Chemical Physics. 1984;80(9):4403-9.
79. Li J, Wu N. Semiconductor-based photocatalysts and photoelectrochemical cells for solar fuel generation: a review. Catalysis Science & Technology. 2015;5(3):1360-84.
80. Liu B, Zhao X, Terashima C, Fujishima A, Nakata K. Thermodynamic and kinetic analysis of heterogeneous photocatalysis for semiconductor systems. Physical Chemistry Chemical Physics. 2014;16(19):8751-60.
81. Corma A, Garcia H. Photocatalytic reduction of CO_2 for fuel production: Possibilities and challenges. Journal of Catalysis. 2013;308:168-75.
82. Carp O, Huisman CL, Reller A. Photoinduced reactivity of titanium dioxide. Progress in Solid State Chemistry. 2004;32(1):33-177.
83. Ola O, Maroto-Valer MM. Review of material design and reactor engineering on TiO_2 photocatalysis for CO_2 reduction. Journal of Photochemistry and Photobiology C: Photochemistry Reviews. 2015;24:16-42.
84. Jiang Z, Xiao T, Kuznetsov Vá, Edwards Pá. Turning carbon dioxide into fuel. Philosophical Transactions of the Royal Society of London A: Mathematical, Physical and Engineering Sciences. 2010;368(1923):3343-64.

85. Lee C-W, Kourounioti RA, Wu JC, Murchie E, Maroto-Valer M, Jensen OE, et al. Photocatalytic conversion of CO_2 to hydrocarbons by light-harvesting complex assisted Rh-doped TiO_2 photocatalyst. Journal of CO_2 Utilization. 2014;5:33-40.
86. Li F, Zhang L, Tong J, Liu Y, Xu S, Cao Y, et al. Photocatalytic CO_2 conversion to methanol by Cu_2O/graphene/TNA heterostructure catalyst in a visible-light-driven dual-chamber reactor. Nano Energy. 2016;27:320-9.
87. Costentin C, Robert M, Savéant J-M. Catalysis of the electrochemical reduction of carbon dioxide. Chemical Society Reviews. 2013;42(6):2423-36.
88. Schwarz H, Dodson R. Reduction potentials of CO_2 and the alcohol radicals. The Journal of Physical Chemistry. 1989;93(1):409-14.
89. Habisreutinger SN, Schmidt-Mende L, Stolarczyk JK. Photocatalytic reduction of CO_2 on TiO_2 and other semiconductors. Angewandte Chemie International Edition. 2013;52(29):7372-408.
90. Willner I, Maidan R, Mandler D, Duerr H, Doerr G, Zengerle K. Photosensitized reduction of carbon dioxide to methane and hydrogen evolution in the presence of ruthenium and osmium colloids: strategies to design selectivity of products distribution. Journal of the American Chemical Society. 1987;109(20):6080-6.
91. Barton Cole E, Lakkaraju PS, Rampulla DM, Morris AJ, Abelev E, Bocarsly AB. Using a one-electron shuttle for the multielectron reduction of CO_2 to methanol: kinetic, mechanistic, and structural insights. Journal of the American Chemical Society. 2010;132(33):11539-51.
92. Schneider J, Jia H, Muckerman JT, Fujita E. Thermodynamics and kinetics of CO_2, CO, and H^+ binding to the metal centre of CO_2 reduction catalysts. Chemical Society Reviews. 2012;41(6):2036-51.
93. Li X, Wen J, Low J, Fang Y, Yu J. Design and fabrication of semiconductor photocatalyst for photocatalytic reduction of CO_2 to solar fuel. Science China Materials. 2014;57(1):70-100.
94. Karamian E, Sharifnia S. On the general mechanism of photocatalytic reduction of CO_2. Journal of CO_2 Utilization. 2016;16:194-203.
95. Mao J, Li K, Peng T. Recent advances in the photocatalytic CO_2 reduction over semiconductors. Catalysis Science & Technology. 2013;3(10):2481-98.

96. Wood PM. The potential diagram for oxygen at pH 7. Biochemical Journal. 1988;253(1):287-9.
97. Ganesh I. Conversion of carbon dioxide into methanol – a potential liquid fuel: Fundamental challenges and opportunities (a review). Renewable and Sustainable Energy Reviews. 2014;31:221-57.
98. Yuan W, Cheng L, Zhang Y, Wu H, Lv S, Chai L, et al. 2D-Layered Carbon/TiO_2 Hybrids Derived from Ti_3C_2 MXenes for Photocatalytic Hydrogen Evolution under Visible Light Irradiation. Advanced Materials InterfacesVisible-light-induced heterostructured Zn–Al–In mixed metal oxide nanocomposite photocatalysts derived from a single precursor. 2017;4(20):1700577.
99. Bian B, Shi L, Katuri KP, Xu J, Wang P, Saikaly PE. Efficient solar-to-acetate conversion from CO_2 through microbial electrosynthesis coupled with stable photoanode. Applied Energy. 2020;278:115684.
100. Wang R, Shen J, Sun K, Tang H, Liu Q. Enhancement in photocatalytic activity of CO_2 reduction to CH_4 by 0D/2D Au/TiO_2 plasmon heterojunction. Applied Surface Science. 2019;493:1142-9.
101. Pougin A, Dodekatos G, Dilla M, Tüysüz H, Strunk J. Au@ TiO_2 Core–Shell Composites for the Photocatalytic Reduction of CO_2. Chemistry A European Journal. 2018;24(47):12416-25.
102. Tang J-y, Yang D, Zhou W-g, Guo R-t, Pan W-g, Huang C-y. Noble-metal-free molybdenum phosphide co-catalyst loaded graphitic carbon nitride for efficient photocatalysis under simulated irradiation. Journal of Catalysis. 2019;370:79-87.
103. He H, Lin J, Fu W, Wang X, Wang H, Zeng Q, et al. MoS_2/TiO_2 edge-on heterostructure for efficient photocatalytic hydrogen evolution. Advanced Energy Materials. 2016;6(14):1600464.
104. Wang T, Zhao Q, Fu Y, Lei C, Yang B, Li Z, et al. Carbon-Rich Nonprecious Metal Single Atom Electrocatalysts for CO_2 Reduction and Hydrogen Evolution. Small Methods. 2019;3(10):1900210.
105. Li Y, Ding L, Liang Z, Xue Y, Cui H, Tian J. Synergetic effect of defects rich MoS_2 and Ti_3C_2 MXene as cocatalysts for enhanced photocatalytic H_2 production activity of TiO_2. Chemical Engineering Journal. 2020;383:123178.

106. Shi H, Du J, Hou J, Ni W, Song C, Li K, et al. Solar-driven CO_2 conversion over Co^{2+} doped 0D/2D TiO_2/g-C_3N_4 heterostructure: Insights into the role of Co^{2+} and cocatalyst. Journal of CO_2 Utilization. 2020;38:16-23.
107. Vu NN, Kaliaguine S, Do TO. Critical aspects and recent advances in structural engineering of photocatalysts for sunlight-driven photocatalytic reduction of CO_2 into fuels. Advanced Functional Materials. 2019;29(31):1901825.
108. Arora S, Prasad R. An overview on dry reforming of methane: strategies to reduce carbonaceous deactivation of catalysts. RSC Advances. 2016;6(110):108668-88.
109. Wang Z-j, Song H, Pang H, Ning Y, Dao TD, Wang Z, et al. Photo-assisted methanol synthesis via CO_2 reduction under ambient pressure over plasmonic Cu/ZnO catalysts. Applied Catalysis B: Environmental. 2019;250:10-6.
110. Aramouni NAK, Touma JG, Tarboush BA, Zeaiter J, Ahmad MN. Catalyst design for dry reforming of methane: Analysis review. Renewable and Sustainable Energy Reviews. 2018;82:2570-85.
111. Han B, Wei W, Chang L, Cheng P, Hu YH. Efficient visible light photocatalytic CO_2 reforming of CH_4. ACS Catalysis. 2015;6(2):494-7.
112. Kohno Y, Tanaka T, Funabiki T, Yoshida S. Reaction mechanism in the photoreduction of CO_2 with CH_4 over ZrO_2. Physical Chemistry Chemical Physics. 2000;2(22):5302-7.
113. Shi D, Feng Y, Zhong S. Photocatalytic conversion of CH4 and CO2 to oxygenated compounds over Cu/CdS–TiO2/SiO2 catalyst. Catalysis Today. 2004;98(4):505-9.
114. Teramura K, Tanaka T, Ishikawa H, Kohno Y, Funabiki T. Photocatalytic reduction of CO_2 to CO in the presence of H_2 or CH_4 as a reductant over MgO. Journal Physical Chemistry B. 2004;108(1):346-54.
115. Yuliati L, Itoh H, Yoshida H. Photocatalytic conversion of methane and carbon dioxide over gallium oxide. Chemical Physics Letters. 2008;452(1-3):178-82.
116. Mahmodi G, Sharifnia S, Rahimpour F, Hosseini SN. Photocatalytic conversion of CO_2 and CH_4 using ZnO coated mesh: Effect of operational parameters and optimization. Solar Energy Materials and Solar Cells. 2013;111:31-40.
117. Tahir B, Tahir M, Amin NAS. Ag-La loaded protonated carbon nitrides nanotubes (pCNNT) with improved charge separation in a monolithic

honeycomb photoreactor for enhanced bireforming of methane (BRM) to fuels. Applied Catalysis B: Environmental. 2019;248:167-83.

118. Tahir M. Enhanced photocatalytic CO_2 reduction to fuels through bireforming of methane over structured 3D MAX Ti_3AlC_2/TiO_2 heterojunction in a monolith photoreactor. Journal of CO_2 Utilization. 2020;38:99-112.
119. Chen X, Mao SS. Titanium dioxide nanomaterials: synthesis, properties, modifications, and applications. Chemical reviews. 2007;107(7):2891-959.
120. Navalon S, Dhakshinamoorthy A, Álvaro M, Garcia H. Photocatalytic CO_2 reduction using non-titanium metal oxides and sulfides. ChemSusChem. 2013;6(4):562-77.
121. Li K, Peng B, Peng T. Recent advances in heterogeneous photocatalytic CO_2 conversion to solar fuels. ACS Catalysis. 2016;6(11):7485-527.
122. Mohapatra L, Parida K. A review on the recent progress, challenges and perspective of layered double hydroxides as promising photocatalysts. Journal of Materials Chemistry A. 2016;4(28):10744-66.
123. Yu J, Wang K, Xiao W, Cheng B. Photocatalytic reduction of CO_2 into hydrocarbon solar fuels over g-C_3N_4–Pt nanocomposite photocatalysts. Physical Chemistry Chemical Physics. 2014;16(23):11492-501.
124. Shi H, Chen G, Zhang C, Zou Z. Polymeric g-C_3N_4 Coupled with $NaNbO_3$ Nanowires toward Enhanced Photocatalytic Reduction of CO_2 into Renewable Fuel. ACS Catalysis. 2014;4(10):3637-43.
125. He Y, Zhang L, Teng B, Fan M. New Application of Z-Scheme Ag_3PO_4/g-C_3N_4 Composite in Converting CO_2 to Fuel. Environmental Science & Technology. 2015;49(1):649-56.
126. Maeda K, Kuriki R, Ishitani O. Photocatalytic activity of carbon nitride modified with a ruthenium (II) complex having carboxylic-or phosphonic acid anchoring groups for visible-light CO_2 reduction. Chemistry Letters. 2016;45(2):182-4.
127. Guo H, Wan S, Wang Y, Ma W, Zhong Q, Ding J. Enhanced photocatalytic CO_2 reduction over direct Z-scheme $NiTiO_3$/g-C_3N_4 nanocomposite promoted by efficient interfacial charge transfer. Chemical Engineering Journal. 2021;412:128646.
128. Huang Y, Wang K, Guo T, Li J, Wu X, Zhang G. Construction of 2D/2D Bi_2Se_3/g-C3N_4 nanocomposite with High interfacial charge separation and

photo-heat conversion efficiency for selective photocatalytic CO_2 reduction. Applied Catalysis B: Environmental. 2020;277:119232.

129. Hisatomi T, Kubota J, Domen K. Recent advances in semiconductors for photocatalytic and photoelectrochemical water splitting. Chemical Society Reviews. 2014;43(22):7520-35.

130. Bi X, Fan T, Zhang H. Novel Morphology-Controlled Hierarchical Core@Shell Structural Organo-Layered Double Hydroxides Magnetic Nanovehicles for Drug Release. ACS Applied Materials & Interfaces. 2014;6(22):20498-509.

131. Fan G, Li F, Evans DG, Duan X. Catalytic applications of layered double hydroxides: recent advances and perspectives. Chemical Society Reviews. 2014;43(20):7040-66.

132. Khan AI, Ragavan A, Fong B, Markland C, O'Brien M, Dunbar TG, et al. Recent developments in the use of layered double hydroxides as host materials for the storage and triggered release of functional anions. Industrial & Engineering Chemistry Research. 2009;48(23):10196-205.

133. Khan AI, O'Hare D. Intercalation chemistry of layered double hydroxides: recent developments and applications. Journal of Materials Chemistry. 2002;12(11):3191-8.

134. Wang Q, O'Hare D. Recent advances in the synthesis and application of layered double hydroxide (LDH) nanosheets. Chemical Reviews. 2012;112(7):4124-55.

135. Cavani F, Trifirò F, Vaccari A. Hydrotalcite-type anionic clays: Preparation, properties and applications. Catalysis Today. 1991;11(2):173-301.

136. Jia J, Qian C, Dong Y, Li YF, Wang H, Ghoussoub M, et al. Heterogeneous catalytic hydrogenation of CO_2 by metal oxides: defect engineering – perfecting imperfection. Chemical Society Reviews. 2017;46(15):4631-44.

137. Yu J, Wang Q, O'Hare D, Sun L. Preparation of two dimensional layered double hydroxide nanosheets and their applications. Chemical Society Reviews. 2017;46(19):5950-74.

138. Yin H, Tang Z. Ultrathin two-dimensional layered metal hydroxides: an emerging platform for advanced catalysis, energy conversion and storage. Chemical Society Reviews. 2016;45(18):4873-91.

139. Zhao Y, Jia X, Waterhouse GI, Wu LZ, Tung CH, O'Hare D, et al. Layered double hydroxide nanostructured photocatalysts for renewable energy production. Advanced Energy Materials. 2016;6(6).
140. Etacheri V, Di Valentin C, Schneider J, Bahnemann D, Pillai SC. Visible-light activation of TiO_2 photocatalysts: Advances in theory and experiments. Journal of Photochemistry and Photobiology C: Photochemistry Reviews. 2015;25:1-29.
141. Schneider J, Matsuoka M, Takeuchi M, Zhang J, Horiuchi Y, Anpo M, et al. Understanding TiO_2 photocatalysis: mechanisms and materials. Chemical reviews. 2014;114(19):9919-86.
142. Xu S-M, Yan H, Wei M. Band structure engineering of transition-metal-based layered double hydroxides toward photocatalytic oxygen evolution from water: a theoretical–experimental combination study. The Journal of Physical Chemistry C. 2017;121(5):2683-95.
143. Suárez-Quezada M, Romero-Ortiz G, Suárez V, Morales-Mendoza G, Lartundo-Rojas L, Navarro-Cerón E, et al. Photodegradation of phenol using reconstructed Ce doped Zn/Al layered double hydroxides as photocatalysts. Catalysis Today. 2016;271:213-9.
144. Hadnadjev-Kostic M, Vulic T, Marinkovic-Neducin R. Solar light induced rhodamine B degradation assisted by TiO_2–Zn–Al LDH based photocatalysts. Advanced Powder Technology. 2014;25(5):1624-33.
145. Mantilla A, Tzompantzi F, Fernández J, Góngora JD, Mendoza G, Gómez R. Photodegradation of 2, 4-dichlorophenoxyacetic acid using ZnAlFe layered double hydroxides as photocatalysts. Catalysis Today. 2009;148(1-2):119-23.
146. Cho S, Jang JW, Kong Kj, Kim ES, Lee KH, Lee JS. Anion-Doped Mixed Metal Oxide Nanostructures Derived from Layered Double Hydroxide as Visible Light Photocatalysts. Advanced Functional Materials. 2013;23(19):2348-56.
147. Tzompantzi F, Mantilla A, Bañuelos F, Fernández J, Gómez R. Improved photocatalytic degradation of phenolic compounds with ZnAl mixed oxides obtained from LDH materials. Topics in Catalysis. 2011;54(1-4):257-63.
148. Fan G, Sun W, Wang H, Li F. Visible-light-induced heterostructured Zn–Al–In mixed metal oxide nanocomposite photocatalysts derived from a single precursor. Chemical Engineering Journal. 2011;174(1):467-74.

149. Zhao Y, Jia X, Waterhouse GI, Wu LZ, Tung CH, O'Hare D, et al. Layered double hydroxide nanostructured photocatalysts for renewable energy production. Advanced Energy Materials. 2016;6(6):1501974.
150. Lan M, Fan G, Yang L, Li F. Significantly enhanced visible-light-induced photocatalytic performance of hybrid Zn–Cr layered double hydroxide/graphene nanocomposite and the mechanism study. Industrial & Engineering Chemistry Research. 2014;53(33):12943-52.
151. Li H, Li J, Xu C, Yang P, Ng DH, Song P, et al. Hierarchically porous MoS2/CoAl-LDH/HCF with synergistic adsorption-photocatalytic performance under visible light irradiation. Journal of Alloys and Compounds. 2017;698:852-62.
152. Rives V, Angeles Ulibarri Ma. Layered double hydroxides (LDH) intercalated with metal coordination compounds and oxometalates. Coordination Chemistry Reviews. 1999;181(1):61-120.
153. Mori K, Taga T, Yamashita H. Isolated Single-Atomic Ru Catalyst Bound on a Layered Double Hydroxide for Hydrogenation of CO_2 to Formic Acid. ACS Catalysis. 2017;7(5):3147-51.
154. Yong Z, Mata V, Rodrigues AE. Adsorption of carbon dioxide onto hydrotalcite-like compounds (HTlcs) at high temperatures. Industrial & Engineering Chemistry Research. 2001;40(1):204-9.
155. Ahmed N, Shibata Y, Taniguchi T, Izumi Y. Photocatalytic conversion of carbon dioxide into methanol using zinc–copper–M (III)(M= aluminum, gallium) layered double hydroxides. Journal of Catalysis. 2011;279(1):123-35.
156. Iguchi S, Hasegawa Y, Teramura K, Hosokawa S, Tanaka T. Preparation of transition metal-containing layered double hydroxides and application to the photocatalytic conversion of CO_2 in water. Journal of CO_2 Utilization. 2016;15:6-14.
157. Kawamura S, Ahmed N, Carja G, Izumi Y. Photocatalytic conversion of carbon dioxide using Zn–Cu–Ga layered double hydroxides assembled with Cu phthalocyanine: Cu in contact with gaseous reactant is needed for methanol generation. Oil & Gas Science and Technology–Revue d'IFP Energies nouvelles. 2015;70(5):841-52.

158. Miyano M, Zhang H, Yoshiba M, Izumi Y. Selective Photoconversion of Carbon Dioxide into Methanol Using Layered Double Hydroxides at 0.40 MPa. Energy Technology. 2017;5(6):892-900.
159. Li J, Yang YB. New type ternary NiAlCe layered double hydroxide photocatalyst for efficient visible-light photoreduction of CO_2 into CH_4. Materials Research Express. 2018.
160. Ye T, Huang W, Zeng L, Li M, Shi J. CeO_{2-x} platelet from monometallic cerium layered double hydroxides and its photocatalytic reduction of CO_2. Applied Catalysis B: Environmental. 2017;210:141-8.
161. Zhao Y, Chen G, Bian T, Zhou C, Waterhouse GIN, Wu L-Z, et al. Defect-Rich Ultrathin ZnAl-Layered Double Hydroxide Nanosheets for Efficient Photoreduction of CO_2 to CO with Water. Advanced Materials. 2015;27(47):7824-31.
162. Saliba D, Ezzeddine A, Sougrat R, Khashab NM, Hmadeh M, Al-Ghoul M. Cadmium–Aluminum Layered Double Hydroxide Microspheres for Photocatalytic CO_2 Reduction. ChemSusChem. 2016;9(8):800-5.
163. Iguchi S, Teramura K, Hosokawa S, Tanaka T. Photocatalytic conversion of CO_2 in an aqueous solution using various kinds of layered double hydroxides. Catalysis Today. 2015;251:140-4.
164. Iguchi S, Teramura K, Hosokawa S, Tanaka T. Effect of the chloride ion as a hole scavenger on the photocatalytic conversion of CO_2 in an aqueous solution over Ni–Al layered double hydroxides. Physical Chemistry Chemical Physics. 2015;17(27):17995-8003.
165. Iguchi S, Teramura K, Hosokawa S, Tanaka T. Photocatalytic conversion of CO_2 in water using fluorinated layered double hydroxides as photocatalysts. Applied Catalysis A: General. 2016;521:160-7.
166. Tokudome Y, Fukui M, Iguchi S, Hasegawa Y, Teramura K, Tanaka T, et al. Nano LDH catalyst with high CO_2 adsorption capability for photo-catalytic reduction. Journal of Materials Chemistry A. 2018.
167. Luo B, Song R, Jing D. ZnCr LDH nanosheets modified graphitic carbon nitride for enhanced photocatalytic hydrogen production. International Journal of Hydrogen Energy. 2017;42(37):23427-36.

168. Hong J, Zhang W, Wang Y, Zhou T, Xu R. Photocatalytic Reduction of Carbon Dioxide over Self-Assembled Carbon Nitride and Layered Double Hydroxide: The Role of Carbon Dioxide Enrichment. ChemCatChem. 2014;6(8):2315-21.
169. Jo W-K, Kumar S, Tonda S. N-doped C dot/CoAl-layered double hydroxide/g-C_3N_4 hybrid composites for efficient and selective solar-driven conversion of CO_2 into CH_4. Composites Part B: Engineering. 2019;176:107212.
170. He F, Zhu B, Cheng B, Yu J, Ho W, Macyk W. 2D/2D/0D $TiO_2/C_3N_4/Ti_3C_2$ MXene composite S-scheme photocatalyst with enhanced CO_2 reduction activity. Applied Catalysis B: Environmental. 2020;272:119006.
171. Zhou Y, Tian Z, Zhao Z, Liu Q, Kou J, Chen X, et al. High-yield synthesis of ultrathin and uniform Bi_2WO_6 square nanoplates benefitting from photocatalytic reduction of CO_2 into renewable hydrocarbon fuel under visible light. ACS Applied Materials & Interfaces. 2011;3(9):3594-601.
172. Cheng L, Li X, Zhang H, Xiang Q. Two-dimensional transition metal MXene-based photocatalysts for solar fuel generation. The journal of Physical Chemistry Letters. 2019;10(12):3488-94.
173. Yang Y, Zhang D, Fan J, Liao Y, Xiang Q. Construction of an Ultrathin S-Scheme Heterojunction Based on Few-Layer g-C_3N_4 and Monolayer $Ti_3C_2T_x$ MXene for Photocatalytic CO_2 Reduction. Solar RRL. 2021;5(2):2000351.
174. Shi Q, Zhang X, Yang Y, Huang J, Fu X, Wang T, et al. 3D hierarchical architecture collaborating with 2D/2D interface interaction in NiAl-LDH/Ti_3C_2 nanocomposite for efficient and selective photoconversion of CO_2. Journal of Energy Chemistry. 2021;59:9-18.
175. Teramura K, Iguchi S, Mizuno Y, Shishido T, Tanaka T. Photocatalytic conversion of CO_2 in water over layered double hydroxides. Angewandte Chemie. 2012;124(32):8132-5.
176. Zhao Y, Chen G, Bian T, Zhou C, Waterhouse GI, Wu LZ, et al. Defect-rich ultrathin ZnAl-layered double hydroxide nanosheets for efficient photoreduction of CO_2 to CO with water. Advanced Materials. 2015;27(47):7824-31.
177. Jiang H, Katsumata K-i, Hong J, Yamaguchi A, Nakata K, Terashima C, et al. Photocatalytic reduction of CO_2 on Cu_2O-loaded Zn-Cr layered double hydroxides. Applied Catalysis B: Environmental. 2018;224:783-90.

178. Iguchi S, Hasegawa Y, Teramura K, Kidera S, Kikkawa S, Hosokawa S, et al. Drastic improvement in the photocatalytic activity of Ga $_2O_3$ modified with Mg–Al layered double hydroxide for the conversion of CO_2 in water. Sustainable Energy & Fuels. 2017;1(8):1740-7.
179. Kumar S, Isaacs MA, Trofimovaite R, Durndell L, Parlett CM, Douthwaite RE, et al. P25@ CoAl layered double hydroxide heterojunction nanocomposites for CO2 photocatalytic reduction. Applied Catalysis B: Environmental. 2017;209:394-404.
180. Lv M, Liu H. Photocatalytic property and structural stability of CuAl-based layered double hydroxides. Journal of Solid State Chemistry. 2015;227:232-8.
181. Zhao H, Xu J, Liu L, Rao G, Zhao C, Li Y. CO_2 photoreduction with water vapor by Ti-embedded MgAl layered double hydroxides. Journal of CO_2 Utilization. 2016;15:15-23.
182. Guo Q, Zhang Q, Wang H, Liu Z, Zhao Z. Core-shell structured ZnO@ Cu-Zn–Al layered double hydroxides with enhanced photocatalytic efficiency for CO_2 reduction. Catalysis Communications. 2016;77:118-22.
183. Wein LA, Zhang H, Urushidate K, Miyano M, Izumi Y. Optimized photoreduction of CO_2 exclusively into methanol utilizing liberated reaction space in layered double hydroxides comprising zinc, copper, and gallium. Applied Surface Science. 2018.
184. Wang K, Zhang L, Su Y, Shao D, Zeng S, Wang W. Photoreduction of carbon dioxide of atmospheric concentration with water to methane over CoAl-Layered Double Hydroxide nanosheets. Journal of Materials Chemistry A. 2018.
185. Khan MR, Chuan TW, Yousuf A, Chowdhury M, Cheng CK. Schottky barrier and surface plasmonic resonance phenomena towards the photocatalytic reaction: study of their mechanisms to enhance photocatalytic activity. Catalysis Science & Technology. 2015;5(5):2522-31.
186. Qu Y, Duan X. Progress, challenge and perspective of heterogeneous photocatalysts. Chemical Society Reviews. 2013;42(7):2568-80.
187. Wang Q, Dong P, Huang Z, Zhang X. Synthesis of Ag or Pt nanoparticle-deposited TiO_2 nanorods for the highly efficient photoreduction of CO_2 to CH_4. Chemical Physics Letters. 2015;639:11-6.

188. Sun Z, Fang W, Zhao L, Wang H. 3D porous Cu-NPs/g-C_3N_4 foam with excellent CO_2 adsorption and Schottky junction effect for photocatalytic CO_2 reduction. Applied Surface Science. 2020;504:144347.
189. Li HJW, Zhou H, Chen K, Liu K, Li S, Jiang K, et al. Metallic MoO_2-Modified Graphitic Carbon Nitride Boosting Photocatalytic CO_2 Reduction via Schottky Junction. Solar RRL. 2020;4(8):1900416.
190. Xu Y-F, Yang M-Z, Chen H-Y, Liao J-F, Wang X-D, Kuang D-B. Enhanced solar-driven gaseous CO_2 conversion by $CsPbBr_3$ nanocrystal/Pd nanosheet Schottky-junction photocatalyst. ACS Applied Energy Materials. 2018;1(9):5083-9.
191. Low J, Yu J, Jaroniec M, Wageh S, Al-Ghamdi AA. Heterojunction photocatalysts. Advanced materials. 2017;29(20):1601694.
192. Matavos-Aramyan S, Soukhakian S, Jazebizadeh MH, Moussavi M, Hojjati MR. On engineering strategies for photoselective CO_2 reduction–A thorough review. Applied Materials Today. 2020;18:100499.
193. Kong XY, Lee WQ, Mohamed AR, Chai S-P. Effective steering of charge flow through synergistic inducing oxygen vacancy defects and pn heterojunctions in 2D/2D surface-engineered Bi_2WO_6/BiOI cascade: Towards superior photocatalytic CO_2 reduction activity. Chemical Engineering Journal. 2019;372:1183-93.
194. Karamian E, Sharifnia S. Enhanced visible light photocatalytic activity of $BiFeO_3$-ZnO p-n heterojunction for CO_2 reduction. Materials Science and Engineering: B. 2018;238-239:142-8.
195. Liu L, Zhang Y, Huang H. Junction Engineering for Photocatalytic and Photoelectrocatalytic CO_2 Reduction. Solar RRL. 2021;5(2):2000430.
196. Zhang L, Jaroniec M. Toward designing semiconductor-semiconductor heterojunctions for photocatalytic applications. Applied Surface Science. 2018;430:2-17.
197. Hasija V, Kumar A, Sudhaik A, Raizada P, Singh P, Van Le Q, et al. Step-scheme heterojunction photocatalysts for solar energy, water splitting, CO_2 conversion, and bacterial inactivation: a review. Environmental Chemistry Letters. 2021:1-26.
198. Iwase A, Yoshino S, Takayama T, Ng YH, Amal R, Kudo A. Water splitting and CO_2 reduction under visible light irradiation using Z-scheme systems

consisting of metal sulfides, CoO_x-loaded $BiVO_4$, and a reduced graphene oxide electron mediator. Journal of the American Chemical Society. 2016;138(32):10260-4.

199. Li J-M, Tsao C-W, Fang M-J, Chen C-C, Liu C-W, Hsu Y-J. TiO2-Au-Cu_2O photocathodes: Au-mediated Z-scheme charge transfer for efficient solar-driven photoelectrochemical reduction. ACS Applied Nano Materials. 2018;1(12):6843-53.

200. He Y, Zhang L, Fan M, Wang X, Walbridge ML, Nong Q, et al. Z-scheme SnO_{2-x}/g-C_3N_4 composite as an efficient photocatalyst for dye degradation and photocatalytic CO_2 reduction. Solar Energy Materials and solar cells. 2015;137:175-84.

201. Jiang Z, Wan W, Li H, Yuan S, Zhao H, Wong PK. A Hierarchical Z-Scheme α-Fe_2O_3/g-C_3N_4 Hybrid for Enhanced Photocatalytic CO_2 Reduction. Advanced materials. 2018;30(10):1706108.

202. Xu Q, Zhang L, Cheng B, Fan J, Yu J. S-Scheme Heterojunction Photocatalyst. Chem. 2020;6(7):1543-59.

203. Wang Z, Chen Y, Zhang L, Cheng B, Yu J, Fan J. Step-scheme CdS/TiO_2 nanocomposite hollow microsphere with enhanced photocatalytic CO_2 reduction activity. Journal of Materials Science & Technology. 2020;56:143-50.

204. Tang Q, Sun Z, Deng S, Wang H, Wu Z. Decorating g-C_3N_4 with alkalinized Ti_3C_2 MXene for promoted photocatalytic CO_2 reduction performance. Journal of Colloid and Interface Science. 2020;564:406-17.

205. Wu Y, Wang H, Sun Y, Xiao T, Tu W, Yuan X, et al. Photogenerated charge transfer via interfacial internal electric field for significantly improved photocatalysis in direct Z-scheme oxygen-doped carbon nitrogen/CoAl-layered double hydroxide heterojunction. Applied Catalysis B: Environmental. 2018;227:530-40.

206. Dinari M, Momeni MM, Ghayeb Y. Photodegradation of organic dye by ZnCrLa-layered double hydroxide as visible-light photocatalysts. Journal of Materials Science: Materials in Electronics. 2016;27(9):9861-9.

207. De Lasa HI, Serrano B, Salaices M. Photocatalytic reaction engineering: Springer; 2005.

208. Yue P. Introduction to the Modelling and Design of Photoreactors. Photoelectrochemistry, Photocatalysis and Photoreactors: Springer; 1985. p. 527-47.
209. Ibhadon AO, Fitzpatrick P. Heterogeneous photocatalysis: recent advances and applications. Catalysts. 2013;3(1):189-218.
210. Mukherjee PS, Ray AK. Major challenges in the design of a large-scale photocatalytic reactor for water treatment. Chemical Engineering and Technology. 1999;22(3):253.
211. Asi MA, He C, Su M, Xia D, Lin L, Deng H, et al. Photocatalytic reduction of CO_2 to hydrocarbons using AgBr/TiO_2 nanocomposites under visible light. Catalysis Today. 2011;175(1):256-63.
212. Wang J-C, Yao H-C, Fan Z-Y, Zhang L, Wang J-S, Zang S-Q, et al. Indirect Z-scheme BiOI/g-C_3N_4 photocatalysts with enhanced photoreduction CO_2 activity under visible light irradiation. ACS Applied Materials & Interfaces. 2016;8(6):3765-75.
213. Zhang Z, Huang Z, Cheng X, Wang Q, Chen Y, Dong P, et al. Product selectivity of visible-light photocatalytic reduction of carbon dioxide using titanium dioxide doped by different nitrogen-sources. Applied Surface Science. 2015;355:45-51.
214. Sayama K, Arakawa H. Photocatalytic decomposition of water and photocatalytic reduction of carbon dioxide over zirconia catalyst. The Journal of Physical Chemistry. 1993;97(3):531-3.
215. Sato S, Arai T, Morikawa T, Uemura K, Suzuki TM, Tanaka H, et al. Selective CO_2 conversion to formate conjugated with H_2O oxidation utilizing semiconductor/complex hybrid photocatalysts. Journal of the American Chemical Society. 2011;133(39):15240-3.
216. Adekoya DO, Tahir M, Amin NAS. g-C_3N_4/(Cu/TiO_2) nanocomposite for enhanced photoreduction of CO_2 to CH_3OH and HCOOH under UV/visible light. Journal of CO_2 Utilization. 2017;18:261-74.
217. Ye Z-G. Handbook of advanced dielectric, piezoelectric and ferroelectric materials: Synthesis, properties and applications: Elsevier; 2008.
218. NoÃ T. Photochemical Processes in Continuous-Flow Reactors: From Engineering Principles to Chemical Applications: World Scientific; 2017.

219. Spadoni G, Bandini E, Santarelli F. Scattering effects in photosensitized reactions. Chemical Engineering Science. 1978;33(4):517-24.
220. Cassano A, Alfano O, Orlando M. Design and analysis of homogeneous and heterogeneous photoreactors. Chemical Engineering Ed Galán, M and del Valle, E John Wiley y Sons, Ltd. 2005:125-69.
221. Merajin MT, Sharifnia S, Hosseini S, Yazdanpour N. Photocatalytic conversion of greenhouse gases (CO_2 and CH_4) to high value products using TiO_2 nanoparticles supported on stainless steel webnet. Journal of the Taiwan Institute of Chemical Engineers. 2013;44(2):239-46.
222. Körbahti BK, Rauf MA. Response surface methodology (RSM) analysis of photoinduced decoloration of toludine blue. Chemical Engineering Journal. 2008;136(1):25-30.
223. Cho I-H, Zoh K-D. Photocatalytic degradation of azo dye (Reactive Red 120) in TiO_2/UV system: Optimization and modeling using a response surface methodology (RSM) based on the central composite design. Dyes and Pigments. 2007;75(3):533-43.
224. Vaez M, Zarringhalam Moghaddam A, Alijani S. Optimization and modeling of photocatalytic degradation of azo dye using a response surface methodology (RSM) based on the central composite design with immobilized titania nanoparticles. Industrial & Engineering Chemistry Research. 2012;51(11):4199-207.
225. Hossain MA, Ayodele BV, Cheng CK, Khan MR. Optimization of renewable hydrogen-rich syngas production from catalytic reforming of greenhouse gases (CH_4 and CO_2) over calcium iron oxide supported nickel catalyst. Journal of the Energy Institute. 2019;92(1):177-94.
226. Ayodele BV, Cheng CK. Modelling and optimization of syngas production from methane dry reforming over ceria-supported cobalt catalyst using artificial neural networks and Box–Behnken design. Journal of Industrial and Engineering Chemistry. 2015;32:246-58.
227. Takanabe K, Nagaoka K, Nariai K, Aika K-i. Titania-supported cobalt and nickel bimetallic catalysts for carbon dioxide reforming of methane. Journal of Catalysis. 2005;232(2):268-75.

228. Jing Q, Fei J, Lou H, Mo L, Zheng X. Effective reforming of methane with CO_2 and O_2 to low H_2/CO ratio syngas over Ni/MgO–SiO_2 using fluidized bed reactor. Energy Conversion and Management. 2004;45(20):3127-37.
229. Fan M-S, Abdullah AZ, Bhatia S. Hydrogen production from carbon dioxide reforming of methane over Ni–Co/MgO–ZrO_2 catalyst: Process optimization. International Journal of Hydrogen Energy. 2011;36(8):4875-86.
230. Rosha P, Singh R, Mohapatra SK, Mahla SK, Dhir A. Optimization of Hydrogen-Enriched Biogas by Dry Oxidative Reforming with Nickel Nanopowder Using Response Surface Methodology. Energy & Fuels. 2018;32(6):6995-7001.
231. Braga TP, Santos RCR, Sales BMC, da Silva BR, Pinheiro AN, Leite ER, et al. CO_2 mitigation by carbon nanotube formation during dry reforming of methane analyzed by factorial design combined with response surface methodology. Chinese Journal of Catalysis. 2014;35(4):514-23.
232. Ayodele BV, Ghazali AA, Mohd Yassin MY, Abdullah S. Optimization of hydrogen production by photocatalytic steam methane reforming over lanthanum modified Titanium (IV) oxide using response surface methodology. International Journal of Hydrogen Energy. 2019;44(37):20700-10.
233. Bloh JZ. A holistic approach to model the kinetics of photocatalytic reactions. Frontiers in Chemistry. 2019;7:128.
234. Mills A, O'Rourke C, Moore K. Powder semiconductor photocatalysis in aqueous solution: An overview of kinetics-based reaction mechanisms. Journal of Photochemistry and Photobiology A: Chemistry. 2015;310:66-105.
235. Tan SS, Zou L, Hu E. Kinetic modelling for photosynthesis of hydrogen and methane through catalytic reduction of carbon dioxide with water vapour. Catalysis Today. 2008;131(1):125-9.
236. Tahir M, Amin NS. Photocatalytic CO_2 reduction and kinetic study over In/TiO_2 nanoparticles supported microchannel monolith photoreactor. Applied Catalysis A: General. 2013;467:483-96.
237. Bafaqeer A, Tahir M, Amin NAS, Mohamed AR, Yunus MAC. Fabricating 2D/2D/2D heterojunction of graphene oxide mediated g-C_3N_4 and ZnV_2O_6 composite with kinetic modelling for photocatalytic CO_2 reduction to fuels under UV and visible light. Journal of Materials Science. 2021;56(16):9985-10007.

238. Thompson WA, Sanchez Fernandez E, Maroto-Valer MM. Review and Analysis of CO_2 Photoreduction Kinetics. ACS Sustainable Chemistry & Engineering. 2020;8(12):4677-92.
239. Mourdikoudis S, Pallares RM, Thanh NT. Characterization techniques for nanoparticles: comparison and complementarity upon studying nanoparticle properties. Nanoscale. 2018;10(27):12871-934.
240. Matović B, Luković J, Nikolić M, Babić B, Stanković N, Jokić B, et al. Synthesis and characterization of nanocrystaline hexagonal boron nitride powders: XRD and luminescence properties. Ceramics International. 2016;42(15):16655-8.
241. Das RS, Agrawal Y. Raman spectroscopy: recent advancements, techniques and applications. Vibrational spectroscopy. 2011;57(2):163-76.
242. Simonescu CM. Application of FTIR spectroscopy in environmental studies. Advanced Aspects of Spectroscopy. 2012:49-84.
243. Kloprogge J, Woodb B, editors. The application of X-ray photoelectron spectroscopy to clay science. Bridging Clays Conference; 2006.
244. Mayeen A, Shaji LK, Nair AK, Kalarikkal N. Chapter 12 - Morphological Characterization of Nanomaterials. In: Mohan Bhagyaraj S, Oluwafemi OS, Kalarikkal N, Thomas S, editors. Characterization of Nanomaterials: Woodhead Publishing; 2018. p. 335-64.
245. Carter M, Shieh JC. Chapter 5 - Microscopy. In: Carter M, Shieh JC, editors. Guide to Research Techniques in Neuroscience. New York: Academic Press; 2010. p. 119-45.
246. Sirita J, Phanichphant S, Meunier FC. Quantitative analysis of adsorbate concentrations by diffuse reflectance FT-IR. Analytical Chemistry. 2007;79(10):3912-8.
247. Erbe A, Nayak S, Chen YH, Niu F, Pander M, Tecklenburg S, et al. How to Probe Structure, Kinetics, and Dynamics at Complex Interfaces In Situ and Operando by Optical Spectroscopy. In: Wandelt K, editor. Encyclopedia of Interfacial Chemistry. Oxford: Elsevier; 2018. p. 199-219.
248. Harriott P. Chemical reactor design: CRC Press; 2002.
249. Tahir M. Construction of a Stable Two-Dimensional MAX Supported Protonated Graphitic Carbon Nitride (pg-C_3N_4)/Ti_3AlC_2/TiO_2 Z-Scheme

Multiheterojunction System for Efficient Photocatalytic CO_2 Reduction through Dry Reforming of Methanol. Energy Fuels. 2020;34(3):3540-56.

250. Bagheri S, Shameli K, Abd Hamid SB. Synthesis and characterization of anatase titanium dioxide nanoparticles using egg white solution via Sol-Gel method. Journal of Chemistry. 2012;2013.

251. Naguib M, Kurtoglu M, Presser V, Lu J, Niu J, Heon M, et al. Two-dimensional nanocrystals produced by exfoliation of Ti_3AlC_2. Advanced Materials. 2011;23(37):4248-53.

252. Nayak S, Parida K. Dynamics of charge-transfer behavior in a plasmon-induced quasi-type-II p–n/n–n dual heterojunction in Ag@ Ag_3PO_4/g-C_3N_4/NiFe LDH nanocomposites for photocatalytic Cr (VI) reduction and phenol oxidation. ACS Omega. 2018;3(7):7324-43.

253. Liu Z, Ma R, Osada M, Iyi N, Ebina Y, Takada K, et al. Synthesis, Anion Exchange, and Delamination of Co−Al Layered Double Hydroxide: Assembly of the Exfoliated Nanosheet/Polyanion Composite Films and Magneto-Optical Studies. Journal of the American Chemical Society. 2006;128(14):4872-80.

254. Zhang Y, Guo B, Hu L, Xu Q, Li Y, Liu D, et al. Synthesis of SnS nanoparticle-modified MXene ($Ti_3C_2T_x$) composites for enhanced sodium storage. Journal of Alloys and Compounds. 2018;732:448-53.

255. Qian Y, Qiao P, Li L, Han H, Zhang H, Chang G. Hydrothermal Synthesis of Lanthanum-Doped MgAl-Layered Double Hydroxide/Graphene Oxide Hybrid and Its Application as Flame Retardant for Thermoplastic Polyurethane. Advances in Polymer Technology 2020;2020:1018093.

256. Xie H, Tang S, Gong Z, Vongehr S, Fang F, Li M, et al. 3D nitrogen-doped graphene/$Co(OH)_2$-nanoplate composites for high-performance electrochemical pseudocapacitors. RSC Advances. 2014;4(106):61753-8.

257. Anbarasan R, Lee W, Im S. Adsorption and intercalation of anionic surfactants onto layered double hydroxides—XRD study. Bulletin of Materials Science. 2005;28(2):145-9.

258. Tahir B, Tahir M, Amin NAS. Photo-induced CO_2 reduction by CH_4/H_2O to fuels over Cu-modified g-C_3N_4 nanorods under simulated solar energy. Applied Surface Science. 2017;419:875-85.

259. Low J, Zhang L, Tong T, Shen B, Yu J. TiO_2/MXene Ti_3C_2 composite with excellent photocatalytic CO_2 reduction activity. Journal of Catalysis. 2018;361:255-66.

260. Zhang X, Liu Y, Dong S, Ye Z, Guo Y. One-step hydrothermal synthesis of a TiO_2-$Ti_3C_2T_x$ nanocomposite with small sized TiO_2 nanoparticles. Ceramics International. 2017;43(14):11065-70.

261. Ye M, Zheng D, Wang M, Chen C, Liao W, Lin C, et al. Hierarchically Structured Microspheres for High-Efficiency Rutile TiO_2-Based Dye-Sensitized Solar Cells. ACS Applied Materials & Interfaces. 2014;6(4):2893-901.

262. Perera SD, Mariano RG, Vu K, Nour N, Seitz O, Chabal Y, et al. Hydrothermal Synthesis of Graphene-TiO_2 Nanotube Composites with Enhanced Photocatalytic Activity. ACS Catalysis. 2012;2(6):949-56.

263. Dias A, Cunha L, Vieira AC. Synthesis and properties of $A_6B_2(OH)16Cl_2{\cdot}4H_2O$ (A=Mg, Ni, Zn, Co, Mn and B=Al, Fe) materials for environmental applications. Materials Research Bulletin. 2011;46(9):1346-51.

264. Pérez-Ramırez J, Mul G, Moulijn J. In situ Fourier transform infrared and laser Raman spectroscopic study of the thermal decomposition of Co–Al and Ni–Al hydrotalcites. Vibrational Spectroscopy. 2001;27(1):75-88.

265. Mo S, Li S, Li J, Deng Y, Peng S, Chen J, et al. Rich surface Co (III) ions-enhanced Co nanocatalyst benzene/toluene oxidation performance derived from Co^{II} Co^{III} layered double hydroxide. Nanoscale. 2016;8(34):15763-73.

266. Vieira AC, Moreira RL, Dias A. Raman Scattering and Fourier Transform Infrared Spectroscopy of $Me_6Al_2(OH)_{16}Cl_2{\cdot}4H_2O$ (Me = Mg, Ni, Zn, Co, and Mn) and $Ca_2Al(OH)_6Cl{\cdot}2H_2O$ Hydrotalcites. The Journal of Physical Chemistry C. 2009;113(30):13358-68.

267. Al-Jaberi M, Naille S, Dossot M, Ruby C. Interlayer interaction in Ca–Fe layered double hydroxides intercalated with nitrate and chloride species. Journal of Molecular Structure. 2015;1102:253-60.

268. Frost RL, Palmer SJ, Theiss F. Synthesis and Raman spectroscopic characterisation of hydrotalcites based on the formula $Ca_6Al_2(CO_3)(OH)_{16}{\cdot}4H_2O$. ournal of Raman Spectroscopy. 2011;42(5):1163-7.

269. Wu L, Hong J, Zhang Q, Chen B-Y, Wang J, Dong Z. Deciphering highly resistant characteristics to different pHs of oxygen vacancy-rich Fe_2Co_1-LDH/PS system for bisphenol A degradation. Chemical Engineering Journal. 2020;385:123620.
270. Jia J, Yang W, Zhang P, Zhang J. Facile synthesis of Fe-modified manganese oxide with high content of oxygen vacancies for efficient airborne ozone destruction. Applied Catalysis A: General. 2017;546:79-86.
271. Liu Y-C, Koza JA, Switzer JA. Conversion of electrodeposited $Co(OH)_2$ to CoOOH and Co_3O_4, and comparison of their catalytic activity for the oxygen evolution reaction. Electrochimica Acta. 2014;140:359-65.
272. Ghule AV, Ghule K, Punde T, Liu J-Y, Tzing S-H, Chang J-Y, et al. In situ monitoring of $NiO–Al_2O_3$ nanoparticles synthesis by thermo-Raman spectroscopy. Materials Chemistry and Physics. 2010;119(1):86-92.
273. Cornaglia LM, Múnera J, Irusta S, Lombardo EA. Raman studies of Rh and Pt on La_2O_3 catalysts used in a membrane reactor for hydrogen production. Applied Catalysis A: General. 2004;263(1):91-101.
274. El Mragui A, Daou I, Zegaoui O. Influence of the preparation method and ZnO/(ZnO+ TiO_2) weight ratio on the physicochemical and photocatalytic properties of ZnO-TiO_2 nanomaterials. Catalysis Today. 2019;321:41-51.
275. Sowmya A, Meenakshi S. Photocatalytic reduction of nitrate over Ag–TiO_2 in the presence of oxalic acid. Journal of Water Process Engineering. 2015;8:e23-e30.
276. Li Y, Xiaobing Z, Wang J, Deng Q, Li M, Du S, et al. Facile preparation of in situ coated $Ti_3C_2T_x$ /$Ni_{0.5}Zn_{0.5}Fe_2O_4$ composites and their electromagnetic performance. RSC Advances. 2017;7:24698-708.
277. Lee E, VahidMohammadi A, Prorok BC, Yoon YS, Beidaghi M, Kim D-J. Room temperature gas sensing of two-dimensional titanium carbide (MXene). ACS Applied Materials & Interfaces. 2017;9(42):37184-90.
278. Pérez-Ramírez J, Mul G, Kapteijn F, Moulijn JA. In situ investigation of the thermal decomposition of Co–Al hydrotalcite in different atmospheres. Journal of Materials Chemistry. 2001;11(3):821-30.
279. Wang K, Zhang L, Su Y, Shao D, Zeng S, Wang W. Photoreduction of carbon dioxide of atmospheric concentration to methane with water over CoAl-layered

double hydroxide nanosheets. Journal of Materials Chemistry A. 2018;6(18):8366-73.

280. Aghazadeh M, Golikand AN, Ghaemi M, Yousefi T. A novel lanthanum hydroxide nanostructure prepared by cathodic electrodeposition. Materials Letters. 2011;65(10):1466-8.

281. Li T, Zhao L, He Y, Cai J, Luo M, Lin J. Synthesis of g-C_3N_4/$SmVO_4$ composite photocatalyst with improved visible light photocatalytic activities in RhB degradation. Applied Catalysis B: Environmental. 2013;129:255-63.

282. Reli M, Huo P, Šihor M, Ambrožová N, Troppová I, Matějová L, et al. Novel TiO_2/C_3N_4 photocatalysts for photocatalytic reduction of CO_2 and for photocatalytic decomposition of N_2O. The Journal of Physical Chemistry A. 2016;120(43):8564-73.

283. Souza ADV, Sousa LL, Fernandes L, Cardoso PHL, Salomão R. Al_2O_3–$Al(OH)_3$-Based castable porous structures. Journal of the European Ceramic Society. 2015;35(6):1943-54.

284. Jagadale AD, Jamadade V, Pusawale S, Lokhande C. Effect of scan rate on the morphology of potentiodynamically deposited β-$Co(OH)_2$ and corresponding supercapacitive performance. Electrochimica Acta. 2012;78:92-7.

285. Jia G, Huang Y, Song Y, Yang M, Zhang L, You H. Controllable synthesis and luminescence properties of La $(OH)_3$ and $La(OH)_3$: Tb^{3+} nanocrystals with multiform morphologies. European Journal of Inorganic Chemistry 2009;2009(25):3721-6.

286. Sun Y, Xiao X, Dong Xa, Dong F, Zhang W. Heterostructured BiOI@$La(OH)_3$ nanorods with enhanced visible light photocatalytic NO removal. Chinese Journal of Catalysis. 2017;38(2):217-26.

287. Salavati-Niasari M, Hosseinzadeh G, Amiri O. Synthesis of monodisperse lanthanum hydroxide nanoparticles and nanorods by sonochemical method. Journal of Cluster Science. 2012;23(2):459-68.

288. Liu Y-C, Koza JA, Switzer JA. Conversion of electrodeposited $Co(OH)_2$ to CoOOH and Co_3O_4, and comparison of their catalytic activity for the oxygen evolution reaction. Electrochim Acta. 2014;140:359-65.

289. Parida K, Satpathy M, Mohapatra L. Incorporation of Fe 3+ into Mg/Al layered double hydroxide framework: effects on textural properties and photocatalytic

activity for H 2 generation. Journal of Materials Chemistry. 2012;22(15):7350-7.

290. Kumar S, Durndell LJ, Manayil JC, Isaacs MA, Parlett CM, Karthikeyan S, et al. Delaminated CoAl-Layered Double Hydroxide@TiO_2 Heterojunction Nanocomposites for Photocatalytic Reduction of CO_2. Particle & Particle System Characterization. 2018;35(1):1700317.

291. Khodakov AY, Chu W, Fongarland P. Advances in the development of novel cobalt Fischer− Tropsch catalysts for synthesis of long-chain hydrocarbons and clean fuels. Chemical Society Reviews. 2007;107(5):1692-744.

292. Jing C, Liu X, Yao H, Yan P, Zhao G, Bai X, et al. Phase and morphology evolution of CoAl LDH nanosheets towards advanced supercapacitor applications. CrystEngComm. 2019;21(33):4934-42.

293. Shao B, Liu Z, Zeng G, Liu Y, Liang Q, He Q, et al. Synthesis of 2D/2D CoAl-LDHs/$Ti_3C_2T_x$ Schottky-junction with enhanced interfacial charge transfer and visible-light photocatalytic performance. Applied Catalysis B: Environmental. 2021;286:119867.

294. Yousaf AB, Imran M, Farooq M, Kasak P. Interfacial Phenomenon and Nanostructural Enhancements in Palladium Loaded Lanthanum Hydroxide Nanorods for Heterogeneous Catalytic Applications. Scientific Reports. 2018;8(1):4354.

295. Shehzad N, Tahir M, Johari K, Murugesan T, Hussain M. Improved interfacial bonding of graphene-TiO_2 with enhanced photocatalytic reduction of CO_2 into solar fuel. Journal of Environmental Chemical Engineering. 2018;6(6):6947-57.

296. Jing C, Huang Y, Xia L, Chen Y, Wang X, Liu X, et al. Growth of cobalt-aluminum layered double hydroxide nanosheets on graphene oxide towards high performance supercapacitors: The important role of layer structure. Applied Surface Science. 2019;496:143700.

297. Zeng H, Deng L, Zhang H, Zhou C, Shi Z. Development of oxygen vacancies enriched CoAl hydroxide@hydroxysulfide hollow flowers for peroxymonosulfate activation: A highly efficient singlet oxygen-dominated oxidation process for sulfamethoxazole degradation. Journal of Hazardous Materials. 2020;400:123297.

298. Yu X, Yin W, Wang T, Zhang Y. Decorating g-C_3N_4 Nanosheets with Ti_3C_2 MXene Nanoparticles for Efficient Oxygen Reduction Reaction. Langmuir. 2019;35(8):2909-16.
299. Li Y, Yin Z, Ji G, Liang Z, Xue Y, Guo Y, et al. 2D/2D/2D heterojunction of Ti3C2 MXene/MoS2 nanosheets/TiO2 nanosheets with exposed (001) facets toward enhanced photocatalytic hydrogen production activity. Applied Catalysis B: Environmental. 2019;246:12-20.
300. Liu Q, Ai L, Jiang J. MXene-derived TiO_2@C/g-C_3N_4 heterojunctions for highly efficient nitrogen photofixation. Journal of Materials Chemistry. 2018;6(9):4102-10.
301. Peng C, Yang X, Li Y, Yu H, Wang H, Peng F. Hybrids of two-dimensional Ti-$_3C_2$ and TiO_2 exposing {001} facets toward enhanced photocatalytic activity. ACS Applied Materials & Interfaces. 2016;8(9):6051-60.
302. Chen L, He B-Y, He S, Wang T-J, Su C-L, Jin Y. Fe—Ti oxide nano-adsorbent synthesized by co-precipitation for fluoride removal from drinking water and its adsorption mechanism. Powder Technology. 2012;227:3-8.
303. Diao Y, Yan M, Li X, Zhou C, Peng B, Chen H, et al. In-situ grown of g-C_3N_4/Ti_3C_2/TiO_2 nanotube arrays on Ti meshes for efficient degradation of organic pollutants under visible light irradiation. Colloids and Surfaces A: Physicochemical and Engineering Aspects. 2020;594:124511.
304. Sunding M, Hadidi K, Diplas S, Løvvik O, Norby T, Gunnæs A. XPS characterisation of in situ treated lanthanum oxide and hydroxide using tailored charge referencing and peak fitting procedures. Journal of Electron Spectroscopy and Related Phenomena. 2011;184(7):399-409.
305. Jo W-K, Kumar S, Tonda S. N-doped C dot/CoAl-layered double hydroxide/g-C_3N_4 hybrid composites for efficient and selective solar-driven conversion of CO_2 into CH_4. Compos B Eng. 2019;176:107212.
306. Ma Y, Wang Y, Xie D, Gu Y, Zhu X, Zhang H, et al. Hierarchical MgFe-layered double hydroxide microsphere/graphene composite for simultaneous electrochemical determination of trace Pb(II) and Cd(II). Chemical Engineering Journal. 2018;347:953-62.
307. Low J, Zhang L, Tong T, Shen B, Yu J. TiO_2/MXene Ti_3C_2 composite with excellent photocatalytic CO_2 reduction activity. J Cat. 2018;361:255-66.

308. Mohapatra L, Parida K. Dramatic activities of vanadate intercalated bismuth doped LDH for solar light photocatalysis. Physical Chemistry Chemical Physics. 2014;16(32):16985-96.
309. Jo W-K, Tonda S. Novel CoAl-LDH/g-C_3N_4/RGO ternary heterojunction with notable 2D/2D/2D configuration for highly efficient visible-light-induced photocatalytic elimination of dye and antibiotic pollutants. Journal of Hazardous Materials. 2019;368:778-87.
310. Rudolf C, Dragoi B, Ungureanu A, Chirieac A, Royer S, Nastro A, et al. NiAl and CoAl materials derived from takovite-like LDHs and related structures as efficient chemoselective hydrogenation catalysts. Catalysis Science & Technology. 2014;4(1):179-89.
311. Eniola JO, Kumar R, Al-Rashdi AA, Ansari MO, Barakat MA. Fabrication of Novel Al $(OH)_3$/CuMnAl-Layered Double Hydroxide for Detoxification of Organic Contaminants from Aqueous Solution. ACS Omega. 2019;4(19):18268-78.
312. Xu H, Li S, Ge L, Han C, Gao Y, Dai D. In-situ synthesis of novel plate-like $Co(OH)_2$ co-catalyst decorated TiO_2 nanosheets with efficient photocatalytic H_2 evolution activity. International Journal of Hydrogen Energy. 2017;42(36):22877-86.
313. Dong F, Xiao X, Jiang G, Zhang Y, Cui W, Ma J. Surface oxygen-vacancy induced photocatalytic activity of $La(OH)_3$ nanorods prepared by a fast and scalable method. Physical Chemistry Chemical Physics. 2015;17(24):16058-66.
314. Eniola JO, Kumar R, Al-Rashdi AA, Ansari MO, Barakat MA. Fabrication of Novel $Al(OH)_3$/CuMnAl-Layered Double Hydroxide for Detoxification of Organic Contaminants from Aqueous Solution. ACS omega. 2019;4(19):18268-78.
315. Kumar S, Isaacs MA, Trofimovaite R, Durndell L, Parlett CMA, Douthwaite RE, et al. P25@CoAl layered double hydroxide heterojunction nanocomposites for CO_2 photocatalytic reduction. Applied Catalysis B: Environmental. 2017;209:394-404.
316. Kim SJ, Lee Y, Lee DK, Lee JW, Kang JK. Efficient Co–Fe layered double hydroxide photocatalysts for water oxidation under visible light. Journal of Materials Chemistry A. 2014;2(12):4136-9.

317. Tonda S, Kumar S, Bhardwaj M, Yadav P, Ogale S. g-C_3N_4/NiAl-LDH 2D/2D hybrid heterojunction for high-performance photocatalytic reduction of CO_2 into renewable fuels. ACS Appl Mater Interfaces. 2018;10(3):2667-78.
318. Baliarsingh N, Mohapatra L, Parida K. Design and development of a visible light harvesting Ni–Zn/Cr–CO_3^{2-} LDH system for hydrogen evolution. Journal of Materials Chemistry A. 2013;1(13):4236-43.
319. Shi Q, Zhang X, Yang Y, Huang J, Fu X, Wang T, et al. 3D hierarchical architecture collaborating with 2D/2D interface interaction in NiAl-LDH/Ti_3C_2 nanocomposite for efficient and selective photoconversion of CO_2. Journal of Energy Chemistry. 2020.
320. Ran J, Gao G, Li F-T, Ma T-Y, Du A, Qiao S-Z. Ti_3C_2 MXene co-catalyst on metal sulfide photo-absorbers for enhanced visible-light photocatalytic hydrogen production. Nature Communication. 2017;8(1):1-10.
321. Carey PH, Ren F, Hays DC, Gila BP, Pearton SJ, Jang S, et al. Band offsets in ITO/Ga_2O_3 heterostructures. Applied Surface Science. 2017;422:179-83.
322. Selvaraju C, Athavan N, Karthick R. Investigation on structural, morphology and photoluminescence properties of lanthanum doped zinc oxide nanostructure for optical application by co-precipitation method. Journal of Materials Science: Materials in Electronics. 2018;29(13):11553-8.
323. Deus RC, Cortés JA, Ramirez MA, Ponce MA, Andres J, Rocha LSR, et al. Photoluminescence properties of cerium oxide nanoparticles as a function of lanthanum content. Materials Research Bulletin. 2015;70:416-23.
324. Zhuang L, Ge L, Yang Y, Li M, Jia Y, Yao X, et al. Ultrathin iron-cobalt oxide nanosheets with abundant oxygen vacancies for the oxygen evolution reaction. Advanced Materials. 2017;29(17):1606793.
325. Dai B, Zhao B, Xie X, Su T, Fan B, Zhang R, et al. Novel two-dimensional $Ti_3C_2T_x$ MXenes/nano-carbon sphere hybrids for high-performance microwave absorption. Journal of MAterials Chemistry C. 2018;6(21):5690-7.
326. Wierzbicki D, Debek R, Motak M, Grzybek T, Gálvez ME, Da Costa P. Novel Ni-La-hydrotalcite derived catalysts for CO2 methanation. Catalysis Communications. 2016;83:5-8.
327. Xiong X, Zhao Y, Shi R, Yin W, Zhao Y, Waterhouse GIN, et al. Selective photocatalytic CO_2 reduction over Zn-based layered double hydroxides containing tri or tetravalent metals. Science Bulletin. 2020;65(12):987-94.

328. Ahmed N, Shibata Y, Taniguchi T, Izumi Y. Photocatalytic conversion of carbon dioxide into methanol using zinc–copper–M (III)(M= aluminum, gallium) layered double hydroxides. J Catal. 2011;279(1):123-35.
329. Iguchi S, Hasegawa Y, Teramura K, Hosokawa S, Tanaka T. Preparation of transition metal-containing layered double hydroxides and application to the photocatalytic conversion of CO_2 in water. J CO_2 Util. 2016;15:6-14.
330. Zhao Y, Chen G, Bian T, Zhou C, Waterhouse GI, Wu LZ, et al. Defect-rich ultrathin ZnAl-layered double hydroxide nanosheets for efficient photoreduction of CO_2 to CO with water. Adv Mater. 2015;27(47):7824-31.
331. Jiang H, Katsumata K-i, Hong J, Yamaguchi A, Nakata K, Terashima C, et al. Photocatalytic reduction of CO_2 on Cu_2O-loaded Zn-Cr layered double hydroxides. Appl Catal B. 2018;224:783-90.
332. Wang C, Ma B, Xu S, Li D, He S, Zhao Y, et al. Visible-light-driven overall water splitting with a largely-enhanced efficiency over a Cu_2O@ZnCr-layered double hydroxide photocatalyst. Nano Energy. 2017;32:463-9.
333. Wang X, Spörer Y, Leuteritz A, Kuehnert I, Wagenknecht U, Heinrich G, et al. Comparative study of the synergistic effect of binary and ternary LDH with intumescent flame retardant on the properties of polypropylene composites. RSC Advances. 2015;5(96):78979-85.
334. Biagini E, Barontini F, Tognotti L. Devolatilization of Biomass Fuels and Biomass Components Studied by TG/FTIR Technique. Industrial & Engineering Chemistry Research. 2006;45(13):4486-93.
335. Yoshikawa K, Sato H, Kaneeda M, Kondo JN. Synthesis and analysis of CO_2 adsorbents based on cerium oxide. Journal of CO_2 Utilization. 2014;8:34-8.
336. Ullah M, Khan SA, Murtaza G, Khenata R, Ullah N, Omran SB. Electronic, thermoelectric and magnetic properties of La_2NiMnO_6 and La_2CoMnO_6. Journal of Magnetism and Magnetic Materials. 2015;377:197-203.
337. Pan B, Luo S, Su W, Wang X. Photocatalytic CO_2 reduction with H_2O over $LaPO_4$ nanorods deposited with Pt cocatalyst. Applied Catalysis B: Environmental. 2015;168-169:458-64.
338. Su T, Hood ZD, Naguib M, Bai L, Luo S, Rouleau CM, et al. Monolayer $Ti_3C_2T_x$ as an Effective Co-catalyst for Enhanced Photocatalytic Hydrogen Production over TiO_2. ACS Applied Energy Materials. 2019;2(7):4640-51.

339. Kulandaivalu T, Mohamed AR, Ali KA, Mohammadi M. Photocatalytic carbon dioxide reforming of methane as an alternative approach for solar fuel production-a review. Renewable and Sustainable Energy Reviews. 2020;134:110363.

340. Muhammad A, Tahir M, Al-Shahrani SS, Mahmood Ali A, Rather SU. Template free synthesis of graphitic carbon nitride nanotubes mediated by lanthanum (La/g-CNT) for selective photocatalytic CO_2 reduction via dry reforming of methane (DRM) to fuels. Applied Surface Science. 2020;504:144177.

341. Luttrell T, Halpegamage S, Tao J, Kramer A, Sutter E, Batzill M. Why is anatase a better photocatalyst than rutile? - Model studies on epitaxial TiO_2 films. Scientific Reports. 2014;4(1):4043.

342. Su R, Bechstein R, Sø L, Vang RT, Sillassen M, Esbjornsson B, et al. How the anatase-to-rutile ratio influences the photoreactivity of TiO_2. The Journal of Physical Chemistry C. 2011;115(49):24287-92.

343. Bakardjieva S, Šubrt J, Štengl V, Dianez MJ, Sayagues MJ. Photoactivity of anatase–rutile TiO_2 nanocrystalline mixtures obtained by heat treatment of homogeneously precipitated anatase. Applied Catalysis B: Environmental. 2005;58(3-4):193-202.

344. Tahir B, Tahir M, Amin NAS. Silver loaded protonated graphitic carbon nitride (Ag/pg-C3N4) nanosheets for stimulating CO2 reduction to fuels via photocatalytic bi-reforming of methane. Applied Surface Science. 2019;493:18-31.

345. Low J, Zhang L, Tong T, Shen B, Yu J. TiO_2/MXene Ti_3C_2 composite with excellent photocatalytic CO_2 reduction activity. Journal of Catalysis. 2018;361:255-66.

346. Merajin MT, Sharifnia S, Hosseini SN, Yazdanpour N. Photocatalytic conversion of greenhouse gases (CO_2 and CH_4) to high value products using TiO_2 nanoparticles supported on stainless steel webnet. Journal of the Taiwan Institute of Chemical Engineers. 2013;44(2):239-46.

347. Delavari S, Amin NAS, Ghaedi M. Photocatalytic conversion and kinetic study of CO_2 and CH4 over nitrogen-doped titania nanotube arrays. Journal of Cleaner Production. 2016;111:143-54.

348. Inagaki M, Tsumura T, Kinumoto T, Toyoda M. Graphitic carbon nitrides (g-C_3N_4) with comparative discussion to carbon materials. Carbon. 2019;141:580-607.

LIST OF PUBLICATIONS

1. **Azmat Ali Khan**, and Muhammad Tahir. "Recent advancements in engineering approach towards design of photo-reactors for selective photocatalytic CO_2 reduction to renewable fuels."*Journal of CO_2 Utilization* 29 (2019): 205-239. (**Q1, I.F = 5.993)**
2. **Azmat Ali Khan**, Muhammad Tahir, and Abdullah Bafaqeer. "Constructing a stable 2D layered Ti_3C_2 MXene cocatalyst-assisted TiO_2/g-C_3N_4/Ti_3C_2 heterojunction for tailoring photocatalytic bireforming of methane under visible light."*Energy & Fuels* 34.8 (2020): 9810-9828. (**Q2, I.F =3.421)**
3. **Azmat Ali Khan**, and Muhammad Tahir. "Well-designed 2D/2D $Ti_3C_2T_{A/R}$ MXene coupled g-C_3N_4 heterojunction with in-situ growth of anatase/rutile TiO_2 nucleates to boost photocatalytic dry-reforming of methane (DRM) for syngas production under visible light." *Applied Catalysis B: Environmental* 285 (2021): 119777. (**Q1, I.F = 16.683)**
4. **Azmat Ali Khan**, Muhammad Tahir, and Zaki Yamani Zakaria. "Synergistic effect of anatase/rutile TiO_2 with exfoliated $Ti_3C_2T_R$ MXene multilayers composite for enhanced CO_2 photoreduction via dry and bi-reforming of methane under UV–visible light." *Journal of Environmental Chemical Engineering* 9.3 (2021): 105244. (**Q1, I.F = 4.300)**
5. **Azmat Ali Khan**, and Muhammad Tahir. "Synergistic Effect of Co/La in Oxygen Vacancy Rich Ternary CoAlLa Layered Double Hydroxide with Enhanced Reductive Sites for Selective Photoreduction of CO_2 to CH_4."*Energy & Fuel* (2021). (**Q2, I.F =3.421)**
6. Muhammad Tahir, **Azmat Ali Khan**, Sehar Tasleem, Rehan Mansoor, and Wei Keen Fan. 2021. 'Titanium Carbide (Ti_3C_2) MXene as a Promising Co-catalyst for Photocatalytic CO2 Conversion to Energy-Efficient Fuels: A Review', Energy & Fuels. (**Q2, I.F =3.421)**