

**PHOTOTHERMAL STEAM REFORMING OF
METHANOL AT MINIMIZED TEMPERATURE
OVER TITANIUM DIOXIDE MODIFIED WITH
PLASMONIC NANOPARTICLES**

BY

Mohammed Altigani Aldaw Abdalmwla

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This thesis, written by **Mohammed Altigani Aldaw Abdalmwla** under the direction of his thesis advisor and approved by his thesis committee, has been presented and accepted by the Dean of Graduate Studies, in partial fulfillment of the requirements for the degree of **MASTER OF SCIENCE IN CHEMISTRY**.



Dr. Jameel R. Al-Thagfi
Department Chairman



Dr. Suliman Saleh Al-Homidan
Dean of Graduate Studies

Date



Dr. Tarek A. Kandiel



Dr. Khalid R. Alhooshani



Dr. Muhammad Nawaz Tahir



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This work is lovingly dedicated to my parents, whose unwavering support, prayers, and encouragement have been my foundation throughout this journey. Their sacrifices and belief in my abilities have inspired me to reach this milestone.

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TABLE OF CONTENTS

ACKNOWLEDGMENT.....	V
TABLE OF CONTENTS.....	VI
LIST OF TABLES	VIII
LIST OF FIGURES.....	IX
LIST OF ABBREVIATIONS.....	XII
ABSTRACT.....	XIII
ملخص الرسالة.....	XV
1 CHAPTER ONE INTRODUCTION	1
1.1 Thermo-photocatalytic MSR.....	1
1.2 Liquid organic hydrogen carriers (LOHCs)	3
1.3 Methanol as liquid organic hydrogen carriers (LOHCs).....	4
1.4 Fundamentals of plasmonic photothermal catalysis	6
1.5 Objectives of the thesis work	9
CHAPTER TWO MATERIALS AND CHARACTERIZATIONS	11
2.1 Chemicals.....	11
2.2 Synthesis Methodologies	11
2.2.1 Synthesis TiO ₂ Anatase.....	11
2.2.2 Synthesis TiO ₂ Brookite.....	11
2.2.3 Preparation of Au-loaded TiO ₂	12
2.2.4 Synthesis of CuAl-LDH	12
2.2.5 Impregnation (physical and in situ mixing) of TiO ₂ P25 on CuAl-LDH:	13

2.2.6	Reduction of CuAl-LDH and impregnated TiO ₂ P25@CuAl-LDH.....	13
2.3	Characterization	13
2.4	Photothermal Measurements.....	16
CHAPTER THREE RESULTS AND CONCLUSION		18
3.1	Thermo-photocatalytic MSR over TiO ₂ modified with Au nanoparticles	18
3.1.1	Characterization results	18
3.1.2	Thermo-photocatalytic MSR	22
3.1.3	Mechanisms of TPC MSR over Au/TiO ₂ catalyst.	26
3.2	Plasmonic Photothermal (PTC) MSR over TiO ₂ @Cu/Al ₂ O ₃	28
3.2.1	Characterization results	28
3.2.2	Photothermal MSR	33
3.2.3	Mechanism of photothermal MSR process	42
CHAPTER FOUR.....		45
CONCLUSION & FUTURE RECOMMENDATIONS.....		45
4.1	Conclusion.....	45
4.2	Future work	47
REFERENCES		48
VITAE.....		53

LIST OF TABLES

Table 1. 1: MSR performance of various recently reported thermo-photo catalysis.....	9
Table 1. 2: MSR performance of various thermal catalysts.....	9

LIST OF FIGURES

Fig. 1. 1: Catalytic principle and pathway of thermo-photo catalysis. (a) Thermo-assisted photocatalysis. (b) Photo-promoted thermal catalysis. (c) Photothermal effect induced by recombination of charge carriers over semiconductor catalysts. (d) Photo-thermal effect and hot carrier generation induced by the decay of plasmons over plasmonic metal catalysts {Fang, 2022 #28}.	2
Fig. 1. 2: Schematic view on hydrogen storage using the LOHCs system via hydrogenation and dehydrogenation {Rao, 2020 #29}.	3
Fig. 1. 3: The number of publications over the years (2000–2020) was analyzed using the Web of Science (Clarivate Analytics) citation database. The search was conducted with the keywords steam reforming of methanol and further refined to include hydrogen production and catalysts.....	6
Fig. 1. 4: Schematic representations of the hot carrier transfer pathways and photothermal conversion are depicted: (a) The hot electron transfer process occurs at the interface between a plasmonic metal and a semiconductor. (b) The mechanism of indirect hot carrier transfer. (c) The direct transfer mechanism of hot carriers. (d) The photo-induced thermal effect involving a plasmonic metal and semiconductor through plasmonic and excitonic processes. (e) The photothermal conversion process is facilitated by a plasmonic metal. (f) The photothermal conversion process in a semiconductor exhibiting localized surface plasmon resonance (LSPR) properties [17-19]	8
Fig. 2. 1: Williamson-Hall plot of (a) 1.0 wt. % Au/TiO ₂ (A 200 °C), (b) 1.0 wt. % Au/TiO ₂ (A 400 °C) and (c) 1.0 wt. % Au/TiO ₂ (A 600 °C) catalysts.....	14
Fig. 2. 2: Photograph of (a) the complete test system and (b) the photothermal reactor.....	17
Fig. 3. 1: (a) XRD patterns and (b) DRS of pristine and 1.0 wt.% Au-modified TiO ₂ materials, and (c) Raman spectra of TiO ₂ (A-200) and 1.0 wt.% Au/TiO ₂ (A-200) materials.....	19
Fig. 3. 2: Low and high-resolution TEM images of (a-b) 1.0 wt.% Au/TiO ₂ (P25), (c-d) 1.0 wt.% Au/TiO ₂ (Br), and (e-f) 1.0 wt.% Au/TiO ₂ (A), respectively, showing the interface between Au and TiO ₂	20
Fig. 3. 3: XPS spectra of (a) Ti 2p, (b) Au 4f, and (c) O 1s of pure TiO ₂ (A-200) and 1.0 wt.% Au/TiO ₂ (A-200).....	21
Fig. 3. 4: The amount of H ₂ , CO and CO ₂ produced via TPC-MSR over (a) 1.0 wt.% Au/TiO ₂ (P25), (b) 1.0 wt.% Au/TiO ₂ (Br), and (c) 1.0 wt.% Au/TiO ₂ (A-200), respectively at 100 °C.	22

Fig. 3. 5: The amount of H ₂ , CO and CO ₂ produced via TPC-MSR over (a) 1.0 wt.% Au/TiO ₂ (P25), (b) 1.0 wt.% Au/TiO ₂ (Br), and (c) 1.0 wt.% Au/TiO ₂ (A-200), respectively at 150 °C.	23
Fig. 3. 6: Rate of H ₂ and CO ₂ production over different thermo-photocatalysts via MSR at 150 °C.	23
Fig. 3. 7: The effect of calcination temperature on (a) crystallite size and BET surface area, (b) crystallite size and rate of hydrogen evolution, and (c) BET surface area and rate of hydrogen evolution over 1.0 wt.% Au/TiO ₂ (A-200).	24
Fig. 3. 8: (a) Effect of light intensity on the amount of H ₂ produced by TPC-MSR over 1.0 wt.% Au/TiO ₂ (A-200), (b) photothermal (TPC) and thermal (T) MSR over 1.0 wt.% Au/TiO ₂ (A-200) at different temperatures, and (c) The action spectrum of 1.0 wt.% Au/TiO ₂ (A-200).	25
Fig. 3. 9: (a) Arrhenius plot for TPC H ₂ production over 1.0 wt.% Au/TiO ₂ (A-200) and (b) Stability test of 1.0 wt. % Au/TiO ₂ (A-200) under TPC-MSR (each cycle was kept for 120 min).	26
Fig. 3. 10: Schematic representation of the PT-MSR of 1.0 wt. % Au/TiO ₂ (A-200) catalyst.	27
Fig. 3. 11: XRD spectra of TiO ₂ P25, CuAl-LDH, and CuAl-LDH modified with different amounts of TiO ₂ P25 using (a) physical mixing and (b) in-situ adding.	29
Fig. 3. 12: XRD patterns of (a) as-prepared CuAl-LDH, 1.0 wt% TiO ₂ -PM@CuAl-LDH (physical mixing) and 1.0 wt% TiO ₂ -IA@CuAl-LDH (in-situ adding); and (b) R-Cu/Al ₂ O ₃ , 1.0 wt % TiO ₂ -PM@R-Cu/Al ₂ O ₃ , and 1.0 wt % TiO ₂ -IA@R-Cu/Al ₂ O ₃ after reduction.	30
Fig. 3. 13: Low and high-resolution TEM images of (a & b) CuAl-LDH, (c & d) 1.0 wt.% P25@CuAl-LDH, (e & f) R-Cu, and (g & h) 1.0 wt.% P25@R-Cu catalysts respectively.	31
Fig. 3. 14: High-resolution XPS spectra of Cu 2p (a), Al 2p (b), and Ti 2p (c) of CuAl-LDH, R-Cu/Al ₂ O ₃ , 1.0 wt.% TiO ₂ -PM@CuAl-LDH, and 1.0 wt.% TiO ₂ -PM@R-Cu/Al ₂ O ₃ catalysis.	32
Fig. 3. 15: High-resolution XPS spectra of Cu 2p (a), Al 2p (b and c) of CuAl-LDH, R-Cu/Al ₂ O ₃ , 1.0 wt.% TiO ₂ -PM@CuAl-LDH, and 1.0 wt.% TiO ₂ -PM@R-Cu/Al ₂ O ₃ catalysis.	32
Fig. 3. 16: (a) DRS and (b) FT-IR spectra of CuAl-LDH, R-Cu/Al ₂ O ₃ , 1.0 wt.% TiO ₂ - PM@CuAl-LDH, and 1.0 wt.% TiO ₂ @R-Cu/Al ₂ O ₃ catalysts respectively.	33
Fig. 3. 17: (a) Time course of PTC H ₂ and CO ₂ production via MSR over R-Cu/Al ₂ O ₃ and 1.0 wt% TiO ₂ -PM@R-Cu/Al ₂ O ₃ catalysts at a temperature of 200 °C and 1.0 sun illumination, and (b) Comparison of the normalized rates for H ₂ and CO ₂ production over investigated catalysts at same conditions.	34
Fig. 3. 18: Time course of H ₂ and CO ₂ evolution by thermocatalytic (a) and photothermal catalytic (b) MSR over R-Cu/Al ₂ O ₃ at 200 °C.	35

Fig. 3. 19: Normalized rate of H ₂ and CO ₂ production via MSR over 1.0 wt% TiO ₂ -PM@R-Cu/Al ₂ O ₃ catalyst at different temperatures (a) TC-MSR and (b) PTC-MSR under 1.0 sun illumination.....	36
Fig. 3. 20: Time course of H ₂ and CO ₂ evolution by thermal catalytic MSR over 1.0 wt% TiO ₂ -PM@R-Cu/Al ₂ O ₃ at (a) 150, (b) 200, and (c) 250 °C.	36
Fig. 3. 21: Time course of H ₂ and CO ₂ evolution by photothermal catalytic MSR over 1.0 wt% TiO ₂ -PM@R-Cu/Al ₂ O ₃ at (a) 150, (b) 200, and (c) 250 °C.	36
Fig. 3. 22: (a) Influence of the amount of TiO ₂ loaded by (a) physical mixing and (b) in-situ adding on the H ₂ and CO ₂ production via the PTC-MSR.....	40
Fig. 3. 23: (a) Action spectrum and (b) stability test for H ₂ and CO ₂ evolution via PTC-MSR over 1.0 wt% TiO ₂ -PM@R-Cu/Al ₂ O ₃ catalyst.	41
Fig. 3. 24: (a) Illustration for the proposed role of TiO ₂ in the hot carrier-enhanced PTC-MSR over 1.0 wt% TiO ₂ -PM@R-Cu/Al ₂ O ₃ catalyst and (b) Apparent activation energy for the TC-MSR and PTC-MSR processes and (c) Influence of the modification of TiO ₂ with Au on the rate of hydrogen evolution via PTC-MSR process.....	44

LIST OF ABBREVIATIONS

MSR	:	Methanol Steam Reforming
LED	:	Light Emitting Diode
PTC	:	Plasmonic Photothermal Catalysis
TPC	:	Thermo-photocatalysis
TC	:	Thermocatalysis
θ	:	The angle at which constructively interfering X-rays leave a crystal
UV	:	Ultraviolet
FESEM	:	Field-emission Scanning Electron Microscope
XRD	:	X-ray Diffraction
XPS	:	X-ray Photoelectron Spectrometer
EF	:	Fermi level
e-	:	Electron
h+	:	Hole
mol	:	Moles
M	:	Molarity
°C	:	Temperature (degree Celsius)
K	:	Temperature (Kelvin)
DRS	:	Diffused Reflectance Spectroscopy
LOHCs	:	Liquid Organic Hydrogen Carriers
g	:	Gram
h	:	Hour
LSPR	:	Localized Surface Plasmon Resonance
LDH	:	Layered Double Hydroxide
A	:	Anatase
B	:	Brookite

ABSTRACT

Full Name : [Mohammed Altigani Aldaw Abdalmwla]
Thesis Title : [Photothermal steam reforming of methanol steam reforming at minimized temperature over titanium dioxide modified with plasmonic nanoparticles]
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Methanol steam reforming (MSR) represents a promising pathway for sustainable hydrogen production, but the release of hydrogen from methanol remains constrained by the energy-intensive thermocatalytic process. In this study, we investigate the thermo-photocatalytic performance of TiO₂ modified with plasmonic nanoparticles for MSR. The integration of plasmonic nanoparticles enhances the photo-induced reactive charge carriers' separation, thus significantly reducing the activation energy and improving the reaction's kinetics.

This work presents an approach to developing and modifying TiO₂ nanomaterials with plasmonic Au nanoparticles to minimize the thermal input required for MSR. The anatase (A) and brookite (B) phases of TiO₂ have been synthesized and modified with 1.0 wt.% Au. The pristine and modified TiO₂ nanomaterials have been characterized by field-emission scanning electron microscopy (FE-SEM), X-ray diffraction (XRD), diffuse reflectance spectroscopy (DRS), and X-ray photoelectron spectroscopy (XPS). The thermo-photocatalytic catalytic activity toward MSR has been evaluated using a batch reactor.

Demonstrating remarkable efficiency, the most active catalyst (i.e. 1.0 wt.% Au/TiO₂ (A 200 °C) achieved a thermo-photocatalytic hydrogen production rate of $370.0 \text{ mmol } g_{cat}^{-1} h^{-1} W^{-1}$ under UV(A) light at 150 °C. No thermocatalytic activity was observed under the same conditions. A

correlation between crystallinity, surface area, and the hydrogen production rate was conducted, indicating that surface area is the dominant parameter.

A facile method for the synthesis of a 1.0 wt.% $\text{TiO}_2@\text{R-Cu}/\text{Al}_2\text{O}_3$ catalyst was introduced. The visible-light-active 1.0 wt.% $\text{TiO}_2@\text{R-Cu}/\text{Al}_2\text{O}_3$ was obtained by reducing CuAl-layered double hydroxide (CuAl-LDH) nanosheets mixed with 1.0 wt.% of TiO_2 (P25). The formation of plasmonic Cu nanoparticles was confirmed by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and transmission electron microscopy (TEM), diffuse reflectance spectroscopy (DRS), and Infrared spectroscopy (IR). The 1.0 wt.% $\text{TiO}_2@\text{R-Cu}/\text{Al}_2\text{O}_3$ catalyst exhibited exceptional efficiency in the plasmonic photothermal catalytic MSR and could deliver a rate of $153.0 \text{ mmol g}_{\text{cat}}^{-1} \text{ h}^{-1} \text{ W}^{-1}$ under simulated solar light (1.0 sun, AM1.5G) at 200 °C. This rate is significantly higher (by 66%) than that obtained under the same conditions in the absence of light. A synergistic effect between TiO_2 and plasmonic Cu nanoparticles was proposed to explain the improved activity.

This work presents an innovative plasmonic photothermal catalytic method for producing hydrogen via methanol steam reforming, showcasing the significant capabilities of plasmonic photothermal catalysis in chemistry and energy.

ملخص الرسالة

الاسم الكامل: محمد التجاني الضو عبدالمولى

عنوان الرسالة: إعادة التشكيل الضوئي الحراري لبخار الميثانول عند درجات حرارة منخفضة باستخدام ثاني أكسيد التيتانيوم

المعدل بجسيمات نانوية بلازمونية

التخصص: كيمياء فيزيائية

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يمثل إعادة تشكيل الميثانول بالبخر (MSR) مسارًا واعدًا لإنتاج الهيدروجين المستدام. ومع ذلك، يظل إطلاق الهيدروجين من الميثانول مقيّدًا بعملية التحفيز الحراري المستهلكة للطاقة بكثافة. في هذه الرسالة، تم دراسة الأداء الحراري-الضوئي الحفزي لأكسيد التيتانيوم (TiO_2) المعدل بجسيمات نانوية بلازمونية لإعادة تشكيل الميثانول بالبخر. يُعزز دمج الجسيمات النانوية البلازمونية فصل حاملات الشحنات النشطة ضوئيًا، مما يقلل بشكل كبير من طاقة التنشيط ويحسن من حركية التفاعل.

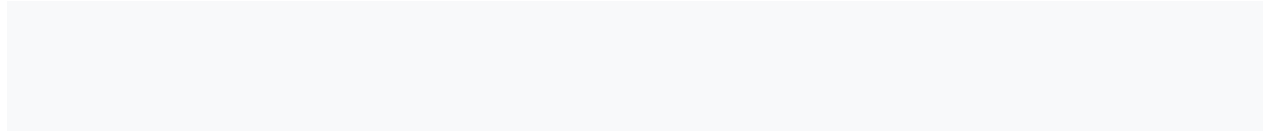
يقدم هذا العمل نهجًا لتطوير وتعديل المواد النانوية من TiO_2 بجسيمات نانوية بلازمونية من الذهب (Au) لتقليل المدخلات الحرارية المطلوبة لإصلاح الميثانول بالبخر. تم تصنيع أطوار الأناتاز (A) والبروكيت (B) من TiO_2 وتعديلها باستخدام 1.0% وزناً من الذهب. تم توصيف المواد النانوية لأكسيد التيتانيوم النقي والمعدل باستخدام مجهر المسح الإلكتروني عالي الدقة (FE-SEM)، وحيود الأشعة السينية (XRD)، ومطيافية الانعكاس المنتشر (DRS)، ومطيافية الأشعة السينية الضوئية (XPS) وتم تقييم النشاط الحراري-الضوئي الحفزي تجاه إعادة تشكيل الميثانول بالبخر.

حققت المحفزات الأكثر نشاطاً ($1.0 \text{ wt.}\% \text{ Au/TiO}_2$ (A 200 °C)) معدل إنتاج هيدروجين حراري-ضوئي حفزي استثنائي بلغ 370.0 ميلي مول $\text{mmol g}^{-1} \text{ h}^{-1} \text{ W}^{-1}$ تحت ضوء الأشعة فوق البنفسجية (UV(A)) عند 150 درجة مئوية ولم يُلاحظ أي نشاط تحفيزي حراري تحت نفس الظروف. تم إجراء علاقة بين التبلور، المساحة السطحية، ومعدل إنتاج الهيدروجين، مما يشير إلى أن المساحة السطحية هي العامل المهيمن.

وقد تم أيضاً تقديم طريقة بسيطة لتصنيع محفز $1.0 \text{ wt.}\% \text{ TiO}_2\text{@R-Cu/Al}_2\text{O}_3$. وتم الحصول على محفز $\text{TiO}_2\text{@R-Cu/Al}_2\text{O}_3$ النشط بالضوء المرئي من خلال صفائح هيدروكسيد النحاس والألمنيوم الطبقي (CuAl-LDH) المخلوطة بنسبة 1.0% وزناً من TiO_2 (P25) وقد تم تأكيد تكوين الجسيمات النانوية البلازمونية للنحاس باستخدام حيود الأشعة السينية (XRD)، ومطيافية الأشعة السينية الضوئية (XPS)، والمجهر الإلكتروني النافذ (TEM)، ومطيافية الانعكاس المنتشر (DRS)، ومطيافية الأشعة تحت الحمراء (IR). أظهر محفز $1.0 \text{ wt.}\% \text{ TiO}_2\text{@R-Cu/Al}_2\text{O}_3$ كفاءة استثنائية في التحفيز الفوتو حراري البلازموني لإعادة تشكيل الميثانول بالبخر، وحقق معدل $153.0 \text{ mmol g}^{-1} \text{ h}^{-1} \text{ W}^{-1}$ تحت ضوء الشمس المحاكي (1.0 sun)

AM1.5G) عند 200 درجة مئوية. هذا المعدل أعلى بشكل ملحوظ (بنسبة 66%) مقارنة بالمعدل الذي تم الحصول عليه في نفس الظروف في غياب الضوء. وتم اقتراح تأثير تآزري بين TiO_2 والجسيمات النانوية البلازمونية للنحاس لتفسير النشاط المحسن.

يقدم هذا العمل طريقة مبتكرة للتحفيز الفوتو حراري البلازموني لإنتاج الهيدروجين عبر إعادة تشكيل الميثانول بالبخار، مما يُبرز القدرات الكبيرة للتحفيز الفوتو حراري البلازموني في الكيمياء والطاقة.



|

CHAPTER ONE

INTRODUCTION

1.1 Thermo-photocatalytic MSR

Thermo-photo catalysis refers to a catalytic process that utilizes both thermal and photo energies synergistically. In this process, thermal energy enhances photocatalysis, while photo energy accelerates thermal catalysis. Thermal energy, which increases the catalyst surface temperature above ambient conditions (25 °C), can be supplied either through external heating sources or generated via light irradiation. Meanwhile, photo-energy is typically provided by laboratory-scale lamps but is envisioned for direct utilization of sunlight in practical applications. It is important to distinguish thermo-photo catalysis from the more commonly discussed photo-thermal catalysis. Photothermal catalysis relies on light-induced temperature increases to achieve desired thermal catalytic performance. In contrast, thermo-photo catalysis encompasses a broader concept, incorporating all interactions and synergies between thermal and photo energies in catalytic processes, including photothermal catalysis [1, 2].

After defining the concept of thermo-photo catalysis, it becomes crucial to accurately and systematically categorize it. Based on catalytic principles, thermo-photo catalysis can be divided into three distinct types: thermo-assisted photocatalysis, photo-enhanced thermal catalysis, and thermo-photo co-catalysis. When photons with energies equal to or greater than the band gap of a catalyst are absorbed, electrons from the valence band are excited to the conduction band, leaving behind holes in the valence band (Step I). These newly generated electrons and holes are anticipated to migrate to the surface of the catalyst (Step II), where they facilitate the reduction

and oxidation reactions of adsorbed reactants, respectively (Step III). However, the recombination of a portion of the electrons and holes is generally unavoidable, see Fig 1.1 [3-8].

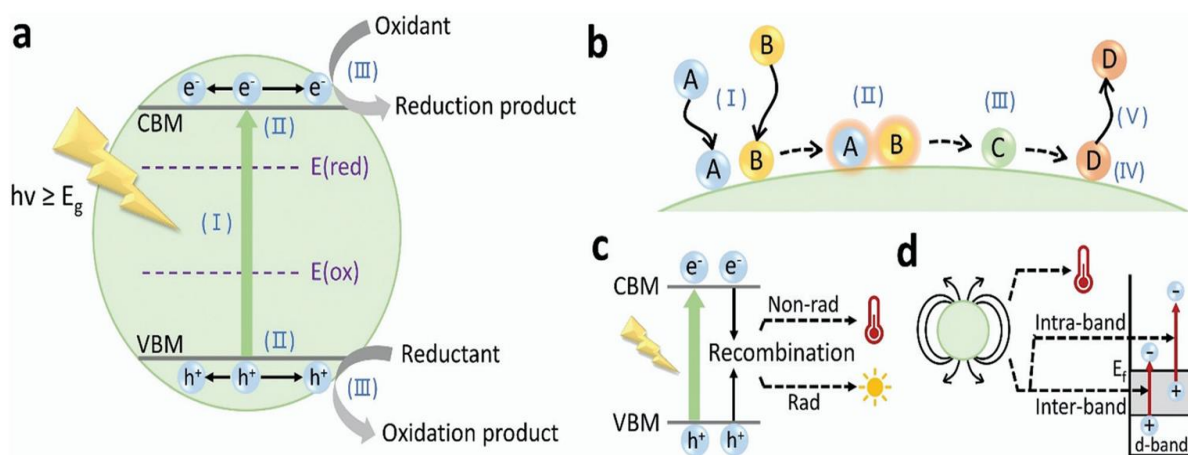


Fig. 1. 1: Catalytic principle and pathway of thermo-photo catalysis. (a) Thermo-assisted photocatalysis. (b) Photo-promoted thermal catalysis. (c) Photothermal effect induced by recombination of charge carriers over semiconductor catalysts. (d) Photo-thermal effect and hot carrier generation induced by the decay of plasmons over plasmonic metal catalysts. Reprinted from ref. [9].

Photothermal catalysis has emerged as a transformative approach to revolutionize MSR by harnessing light energy to drive catalytic reactions. In photothermal MSR, specialized materials convert incident light into localized heat and energetic charge carriers, enabling the reforming reaction at significantly reduced external temperatures. This dual activation mechanism of thermal energy generation and charge transfer reduces the reliance on external heat sources while improving reaction kinetics and selectivity. Photothermal catalysis not only enhances energy efficiency but also minimizes environmental impact, aligning with global goals for sustainable energy production [10, 11].

1.2 Liquid organic hydrogen carriers (LOHCs)

Liquid organic hydrogen carriers (LOHCs) are organic compounds capable of chemically absorbing and releasing hydrogen, making them effective hydrogen storage media. The principle of LOHC-based storage involves a hydrogenation reaction where the dehydrogenated form of the LOHC, typically an unsaturated aromatic compound such as benzene, toluene, naphthalene, or dibenzyltoluene reacts with hydrogen. This exothermic process occurs at elevated pressures (around 30–50 bar) and temperatures (approximately 150–200 °C) in the presence of a catalyst, resulting in the formation of a saturated compound. The saturated LOHC can then be stored or transported under standard ambient conditions. When hydrogen is needed again, the hydrogen-rich form of the LOHC undergoes dehydrogenation, releasing the stored hydrogen. This endothermic process occurs at elevated temperatures (250–320 °C) in the presence of a catalyst. Before use, the released hydrogen may need purification to remove LOHC vapors. To enhance efficiency, the heat from the hot material exiting the release unit should be transferred to the incoming hydrogen-rich LOHC. This preheating minimizes the energy required to prepare the material for the reaction. Additionally, utilizing the heat generated during the hydrogenation process can further improve the system's overall energy efficiency. The heat generated during hydrogen absorption can, in principle, be utilized for heating applications or as process heat.

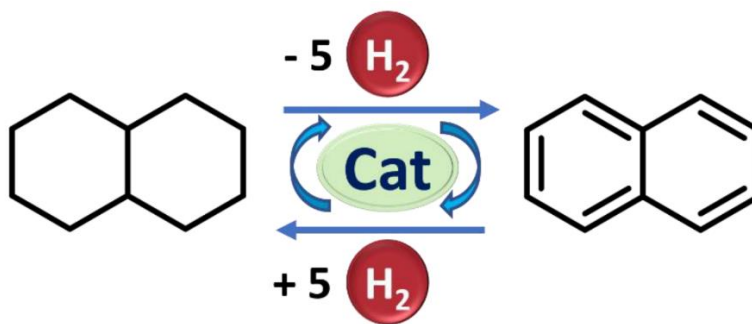
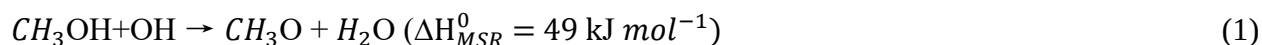


Fig. 1. 2: Schematic view on hydrogen storage using the LOHCs system via hydrogenation and dehydrogenation reprinted from ref. [12].

1.3 Methanol as liquid organic hydrogen carriers (LOHCs)

Methanol (CH_3OH) is regarded as an ideal candidate for LOHCs. Thermocatalytic production of H_2 by methanol steam reforming (MSR) reaction (Eq.1) takes place at high temperature (200–350 °C) with the production of 3 mol of H_2 from 1 mol of CH_3OH .



To achieve highly efficient MSR under milder reaction conditions, both methanol and water molecules need to be activated effectively. Employing solar energy is a novel and sustainable approach for launching this catalytic process at minimized thermal input. Photocatalytic H_2 production from $\text{CH}_3\text{OH}/\text{H}_2\text{O}$ solution has been extensively investigated using particulate semiconductors or photosensitizers coupled with cocatalysts. Still, it is commonly inefficient because of the limitations of photogenerated carriers transfer processes and the poor sunlight-harvesting property of typical photocatalysts in the visible light. Although significant progress has been made recently, the state-of-the-art photocatalytic H_2 production rate from methanol aqueous solution remains at several $\text{mmol g}^{-1} \text{h}^{-1}$ [8], far behind the demands of industrialization. In recent years, titanium dioxide (TiO_2) has garnered significant attention as a catalytic support material due to its excellent chemical stability, low cost, and high surface area. However, the catalytic performance of pure TiO_2 in MSR is relatively low. To enhance its catalytic efficiency, researchers have focused on modifying TiO_2 with noble metal nanoparticles, particularly gold (Au), known for their unique plasmonic properties [13-16]. When deposited on TiO_2 , gold plasmonic nanoparticles can enhance catalytic activity through a phenomenon known as the plasmonic effect. This effect arises from light interaction with the gold nanoparticles' free electrons, leading to localized surface plasmon resonance (LSPR). LSPR can generate localized heat and hot electrons, which can be transferred to the TiO_2 support, thereby boosting its catalytic performance. This

combination of photothermal and photocatalytic effects offers an approach to improving the efficiency of methanol steam reforming. The increasing number of publications highlights the growing interest and attention being directed toward the steam reforming of methanol. This upward trend in research output suggests that the topic is becoming increasingly significant within the scientific community. The volume of publications, conference presentations, and patents related to methanol steam reforming has experienced a remarkable and sustained surge in recent years, as illustrated in Fig. 1.2. This upward trend, which began to accelerate around 1998, reflects a growing global emphasis on fuel cell research, driven by the collaborative efforts of academic institutions, government research laboratories, and industrial sectors. The significant increase in interest stems from the pivotal role of methanol steam reforming in hydrogen production, a key component of advancing fuel cell technologies for cleaner and more sustainable energy systems. This rise in activity also parallels the broader expansion of research and discussions on fuel cells, marked by a substantial increase in specialized publications and the inclusion of dedicated fuel cell symposia within larger professional conferences. Organizations such as AIChE, ACS, ASM, ECS, IECEC, IMRET, and others have played a critical role in fostering this interdisciplinary dialogue and innovation.

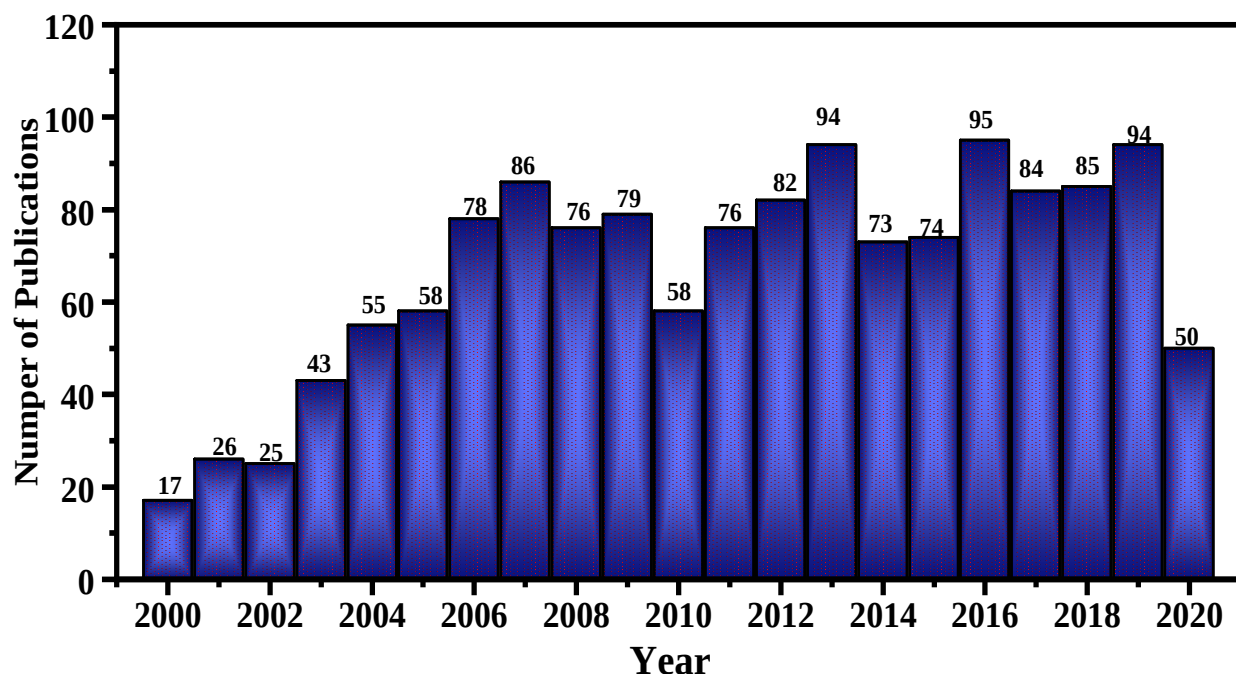


Fig. 1. 3: The number of publications over the years (2000–2020) was analyzed using the Web of Science (Clarivate Analytics) citation database. The search was conducted with the keywords steam reforming of methanol and further refined to include hydrogen production and catalysts.

1.4 Fundamentals of plasmonic photothermal catalysis

Surface plasmon resonance (SPR) is a characteristic optical property of certain metallic nanoparticles, arising from the coherent oscillation of conduction electrons when the frequency of incident photons aligns with the natural oscillation frequency of surface electrons against the positive nuclei's restoring force. Upon intra-band (between the Fermi level and the sp conduction band) [17] or inter-band (between the d band and sp conduction band) excitation of plasmonic nanometals, energetic hot carriers are generated through the dephasing of free electron oscillations via a non-radiative energy dissipation process, known as Landau damping. These hot carriers, if sufficiently energetic, can transfer to the electron-accepting states of nearby surface adsorbates or semiconductors, facilitating surface chemical transformations on femtosecond to picosecond timescales [18-20]. Alternatively, they can dissipate energy as heat through interactions with

phonon modes, occurring over picosecond to nanosecond timescales, which enhances mass transfer and reaction rates [21].

The SPR-mediated catalytic process in plasmonic nanostructures is classified as either plasmonic photocatalysis, dominated by charge carrier activation, or photothermal catalysis, driven by heat generation. By tailoring the optical properties of plasmonic metals—such as the energy of localized SPR (LSPR)—to complement the electronic structure of adsorbates, hot carrier activation and photothermal heat can synergistically enhance catalytic efficiency. This coupling under high-intensity light irradiation enables efficient and selective surface reactions, defining a hybrid process termed plasmonic photothermal catalysis. This mechanism integrates the benefits of both plasmonic photocatalysis and photothermal catalysis, leveraging hot carrier transfer and photothermal conversion to drive reactions [21]. A schematic overview of this process is presented, illustrating the reaction pathways involved.

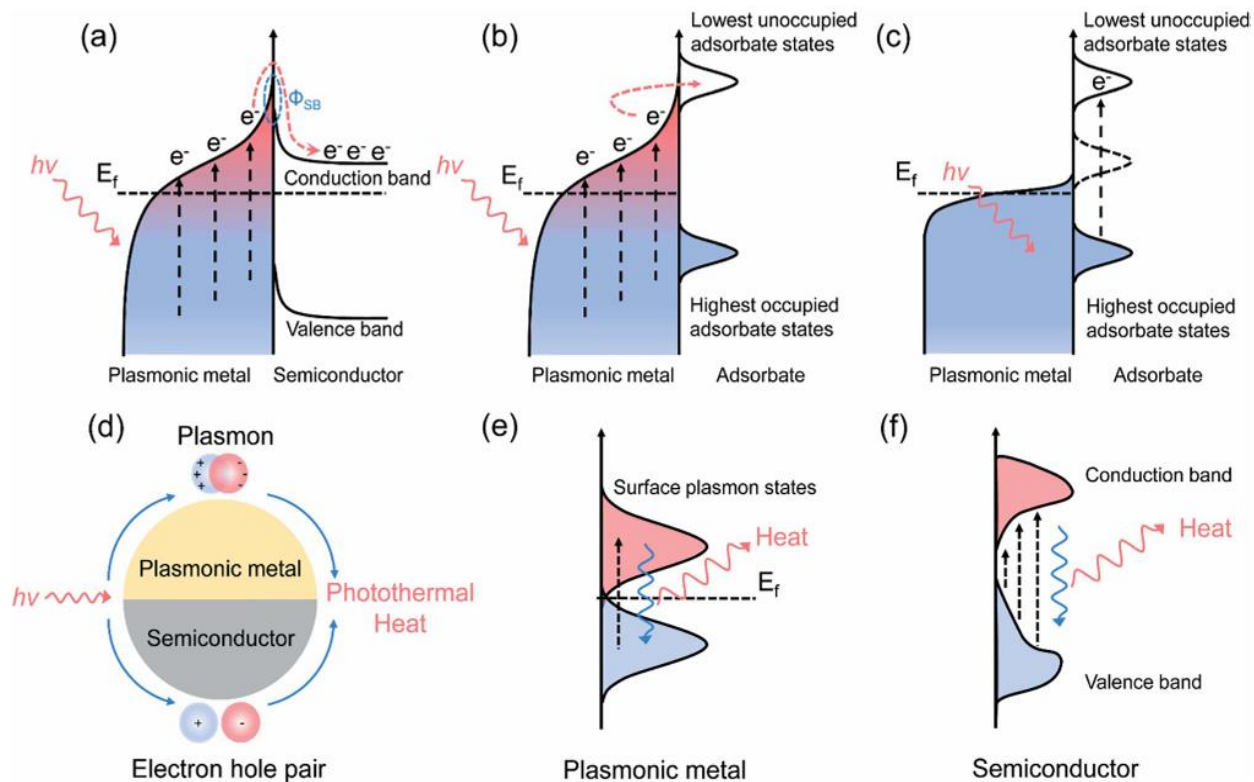


Fig. 1. 4: Schematic representations of the hot carrier transfer pathways and photothermal conversion are depicted: (a) The hot electron transfer process occurs at the interface between a plasmonic metal and a semiconductor. (b) The mechanism of indirect hot carrier transfer. (c) The direct transfer mechanism of hot carriers. (d) The photo-induced thermal effect involving a plasmonic metal and semiconductor through plasmonic and excitonic processes. (e) The photothermal conversion process is facilitated by a plasmonic metal. (f) The photothermal conversion process in a semiconductor exhibiting localized surface plasmon resonance (LSPR) properties. Reprinted from ref [22].

Recently, there has been an increasing emphasis on hydrogen production through photothermal Methanol Steam Reforming (MSR) reactions, reflecting the global push towards sustainable and efficient energy solutions. This method combines the advantages of thermal catalysis and photocatalysis, leveraging both heat and light to enhance the reaction's efficiency. Studies have demonstrated notable differences in hydrogen production rates across various catalytic methods, including purely photocatalytic, thermal catalytic, and photothermal catalytic approaches, as outlined in Table 1. The photothermal approach stands out due to its ability to utilize light energy effectively, leading to enhanced reaction rates and reduced energy consumption. This growing

interest stems from the potential of photothermal MSR to offer a cleaner and more energy-efficient pathway for hydrogen generation, a critical component for fueling fuel cells and other clean energy technologies. Table 1 and 2 highlights the comparative performance of these methods, underscoring the promise of photothermal catalysis in hydrogen production.

Table 1. 1: MSR performance of various recently reported thermo-photo catalysis.

Thermo-photo Catalyst	T (°C)	Light source	H ₂ Rate (mmol g ⁻¹ h ⁻¹ W ⁻¹)	Ref
CuAl-LDH	245	Xe lamp	135	[23]
Zn _{1.3} Cu _{98.7} alloy	235	Focused solar light	95	[24]
1.0 wt %Au/TiO ₂	150	LED 360 nm	55	[25]
Cu/CeO ₂	250	Xe lamp	2	[26]
1.0 wt.% Au/TiO ₂ (A 200 °C)	150	LED 360 nm	370	This work
1.0wt.% TiO ₂ -PM@R-Cu/Al ₂	150	Simulated solar light 1.0 sun, AM 1.5 G	115	This work

Table 1. 2: MSR performance of various thermal catalysts.

Thermal Catalyst	T (°C)	H ₂ Rate (mmol g ⁻¹ h ⁻¹)	Ref
Ni/ α -MoC	240	10.5	[27]
2%Pt/ α -MoC	190	9	[28]
NiAl-Au	340	8.5	[29]
Cu/ZnO/Al ₂ O ₃	250	6.6	[30]
Pt/In ₂ O ₃ /CeO ₂	325	5.7	[31]
Pd/ZnO	200	0.5	[32]
Cu-Ga/ZnO	220	3.65	[33]

1.5 Objectives of the thesis work

The primary goal of this research is to induce the MSR process at minimized temperatures by utilizing TiO_2 modified with plasmonic nanoparticles as photo-thermal catalysts. The detailed objectives are outlined as follows:

- Minimize the temperature of MSR to below 200 °C.
- Achieve complete methanol steam reforming (CO-Free H_2).
- Explore the reaction mechanism of the thermo-photocatalytic MSR process.

CHAPTER TWO

MATERIALS AND CHARACTERIZATIONS

2.1 Chemicals

Titanium tetrachloride (TiCl_4), sodium lactate (50 wt.% in H_2O), Titanium (IV) bis(ammonium lactate) dihydroxide (TALH, 50 wt.% in H_2O), Urea, Dichloromethane (CH_2Cl_2), Thioglycolic acid ($\text{C}_2\text{H}_4\text{O}_2\text{S}$), Tetrachloroauric (III) acid (HAuCl_4), Sodium borohydride (NaBH_4), Copper (II) nitrate trihydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$), Aluminium nitrate nonahydrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), DI water, Sodium hydroxide (NaOH), Sodium carbonate (Na_2CO_3), Titanium dioxide (TiO_2 (P25)). All chemicals were purchased from Sigma-Aldrich and used as received.

2.2 Synthesis Methodologies

2.2.1 Synthesis TiO_2 Anatase

5.0 mL of titanium tetrachloride (TiCl_4) was incrementally added to 30 mL of ice-cold water while stirring to produce a clear TiCl_4 aqueous solution. After 30 minutes of stirring, the TiCl_4 aqueous solution was immediately heated to 120 °C to eliminate water and hydrogen chloride. The resultant white solid was carefully rinsed with DI water, dried in air at 80 °C for 24 hours, and calcined in a muffle furnace at 200, 400, and 600 °C for 2 hours to improve crystallinity. The final products are designated as TiO_2 (A) [34].

2.2.2 Synthesis TiO_2 Brookite

The pure brookite TiO_2 was hydrothermally synthesized by mixing 5.0 mL of a 50% aqueous solution of titanium (IV) bis(ammonium lactate) dihydroxide (TALH) with 5.0 mL of a 50% aqueous sodium lactate solution. Then, the final volume was adjusted to 50 mL by adding 40 mL of a 6.0 M urea solution and transferred into a 100 mL Teflon-cup-lined autoclave. The autoclave

was securely sealed and placed in an oven at 180 °C for 24 hours. Subsequently, the autoclave was allowed to cool naturally to ambient temperature. The TiO₂ nanomaterials underwent centrifugation and were rinsed twice with DI water, once with ethanol, and dried in an oven overnight at 70 °C. The thoroughly desiccated solid was pulverized using an agate mortar and subsequently calcined at 500 °C for 2 hours to eliminate the organic chemicals adsorbed on the surface. The resultant powder was subsequently designated as TiO₂(Br) [35].

2.2.3 Preparation of Au-loaded TiO₂

Au/TiO₂ with Au-NP loadings (1.0 wt. %) were prepared according to the reported method [36]. 0.25 g of TiO₂ (P25, B, and A) was suspended in 50 mL dichloromethane (CH₂Cl₂), and then 1.2 mL of thioglycolic acid (C₂H₄O₂S) was added to it and stirred for 2h. Then, the resultant mixture was washed with dichloromethane, centrifuged, and overnight dried in an oven at 65 °C. The above thiol functionalized TiO₂ (P25, B, and A) was then suspended with 50 mL DI water. Then, 5.0 µL of HAuCl₄ solution (0.025 M) was added to this suspension under vigorous stirring for a gold content of 1.0 %. The Au (III) ions were reduced by 10 mL of a 0.1 M NaBH₄ aqueous solution. The colour of the solution changed to violet, indicating the reduction of Au (III) to Au (0). It was maintained under vigorous stirring at room temperature for 2 h. Afterward, the solid was washed three times thoroughly with DI water, centrifuged, and then dried at 60 °C 12h. The final production is named 1.0 wt. % Au/TiO₂ (P25, Br and A)

2.2.4 Synthesis of CuAl-LDH

CuAl-LDH nanosheets were synthesized via a co-precipitation method[37], with a Cu: Al molar ratio of 3:1. Solution A was formulated by dissolving 3.62 g (15 mmol) of Cu(NO₃)₂·3H₂O and 1.88 g (5 mmol) of Al(NO₃)₃·9H₂O in 20 mL of DI water. Solution B was prepared by dissolving 1.8 g (45 mmol) of NaOH in 30 mL of DI water. Both solutions (A and B) were added one by one

to a three-necked flask containing 180 mL of 10 mmol Na₂CO₃ solution. The solutions were mixed continuously while keeping the pH at 9.5. The resultant combination was then cooked at 65 °C for 13 h. The solid product was centrifuged, followed by several washes with DI water. It was then dried at 60 °C under a vacuum for 24 h.

2.2.5 Impregnation (physical and in situ mixing) of TiO₂ P25 on CuAl-LDH:

For physical mixing modification, the TiO₂ P25 is physically mixed with the synthesized CuAl-LDH with weight % of 0.5, 1.0, 2.5, 5.0, 7.5, 10.0, and 50.0. For in-situ modification, the TiO₂ P25 was added with weight % of 0.5, 1.0, 2.5, 5.0, 7.5, 10.0, and 50.0 during the synthesis of CuAl-LDH.

2.2.6 Reduction of CuAl-LDH and impregnated TiO₂ P25@CuAl-LDH

The R-Cu/Al₂O₃ and TiO₂@R-Cu/Al₂O₃ were derived from CuAl-LDH nanosheets and TiO₂@CuAl-LDH, respectively, by reduction in an H₂/Ar (10/90 v/v) environment at a temperature of 300 °C for 4 h. After the reduction process, the resulting product was allowed to cool gradually to room temperature in the presence of Ar flow.

2.3 Characterization

X-ray Diffraction (XRD): The powder X-ray diffraction (XRD) patterns were obtained using a Rigaku diffractometer operating in reflection mode with CuK α radiation ($\lambda = 0.15406$ nm) at an accelerating voltage of 40 kV. Data were collected in the 2θ angular range of 10° to 80° with a step size of 0.02°. To determine the crystallite size, the observed XRD peak broadening (β_m) at the full width at half maximum (FWHM) was adjusted for instrumental broadening using the following equation (2-3):

$$\beta_d^2 = \beta_m^2 - \beta_i^2 \quad (2)$$

Here, β_d represents the corrected peak broadening, and β_i denotes the instrumental broadening. Crystalline silicon was utilized as a standard reference material for position calibration and determining instrumental broadening. The crystallite size was then estimated using the Williamson-Hall plot and the following equation:

$$\beta_{hkl} \cos \theta_{hkl} = \frac{K\lambda}{D} + 4\varepsilon \sin \theta_{hkl} \quad (3)$$

In this context, β_d refers to the corrected peak broadening, while β_i corresponds to the instrumental broadening. K is the shape factor (0.9). Crystalline silicon served as a standard reference material for calibrating peak positions and calculating instrumental broadening. The crystallite size was subsequently determined using the Williamson-Hall plot and the equation below:

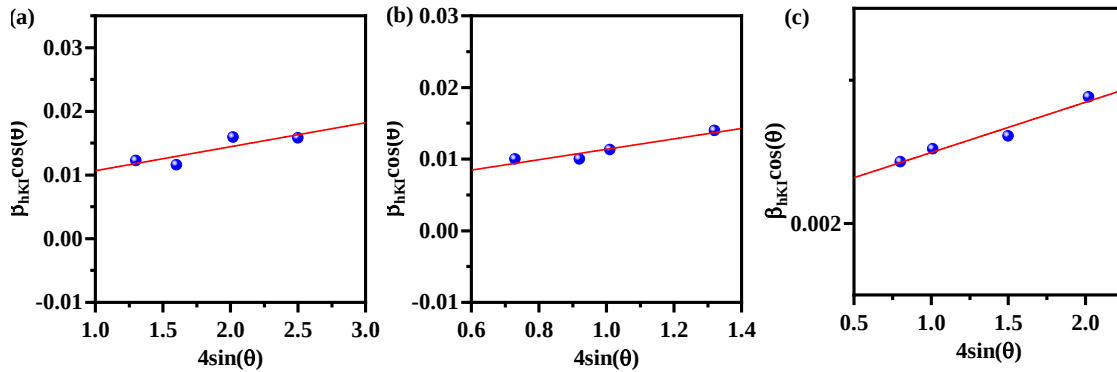


Fig. 2. 1: Williamson-Hall plot of (a) 1.0 wt. % Au/TiO₂ (A 200 °C), (b) 1.0 wt. % Au/TiO₂ (A 400 °C) and (c) 1.0 wt. % Au/TiO₂ (A 600 °C) catalysts.

Field Emission Scanning Electron Microscope (FE-SEM): FE-SEM measurements were carried out by the TESCAN field emission microscope operating at an accelerating voltage of 15 kV. The focused beam of high-energy electrons is utilized for high-resolution images of the surface of the materials. In FE-SEM, a high-energy beam of electrons is generated and accelerated by the high voltage (1–30 kV). When this high-energy electron beam strikes the sample, it penetrates the

sample for a few microns to produce different signals. The secondary and backscattered electrons are collected by the detector and combined to produce high-resolution images on the screen. For EDS measurements the LINKINCA program system was attached to the FE-SEM to find out the elemental composition of the sample. The X-ray detector is positioned in such a way that X-rays emitted by the sample are intercepted. This generates a small current which is further changed into the voltage pulse and the size of this pulse is proportional to the frequency of the X-rays.

X-ray Photoelectron Spectroscopy (XPS): The X-ray photoelectron spectroscopy (XPS) examination was conducted using the ESCALAB™ Xi⁺ X-ray photoelectron spectrometer manufactured by Thermo Scientific. This spectrometer utilized a monochromatic micro-focused Al K α X-ray source for the XPS investigation. The calibration of the XPS spectra was performed using the C 1s peak at 284.8 eV as a reference standard.

UV-Vis Diffuse Reflectance Spectroscopy (UV-Vis DRS): The Shimadzu (UV-3600i) UV-Vis-NIR spectrophotometer was used to analyze the UV Vis diffuse reflectance spectra (DRS) of all electrodes with BaSO₄ as a reference.

Raman Spectroscopy: The Raman spectroscopy analysis of the materials was conducted using the HORIBA Scientific LabRAM HR Evolution Raman spectrometer. This instrument was equipped with an internal He-Ne laser emitting a red light with a power output of 17 mW and an excitation wavelength of 633 nm. A 10x objective lens was used to focus the laser on photoanode films. The acquisition time of 25 s with 2 accumulation was set for the Raman spectra collection.

Field-Emission Transmission Electron Microscope (FE-TEM): FE-TEM (JEM-F200, Jeol) operated at 200 kV was employed for collecting the TEM images.

2.4 Photothermal Measurements

The MSR test was conducted in a stainless-steel reactor with a capacity of 50 cm³ using the Perfectlight system (Scheme 1a). The reactor is adapted with a quartz glass window to allow light irradiation. In a typical test, 4.0 mg of catalyst was dispersed in DI water, sonicated, and immobilized on microscope glass with a defined area of 4.0 cm² using the doctor blading method. The sample was then dried and transferred to the reactor and positioned on the heat plate. The reactor was then purged with He to remove the air, and subsequently, 500 µL of CH₃OH/H₂O mixture with a 1:1 v/v ratio was injected into the reactor through the sample port. The temperature was adjusted to the desired value using the temperature controller. The temperature sensor was kept close to the catalyst surface, as shown in Fig 2.2. A SunLite solar simulator from Abet Technologies was used as a light source. The light intensity was adjusted to 1.0 sun using a calibrated silicon reference cell. The gases produced during the MSR process were analyzed by Shimadzu Nexis GC-2030 gas chromatograph (GC) equipped with a BID detector. The carrier gas was Helium (He). The apparent quantum efficiency (AQE) of catalysts was calculated from the equations (4-5):

$$\% AQE = \frac{2 \times n_{H_2} \times N_A}{N_{ph}} \times 100 \quad (4)$$

Where N_A is Avogadro's number, n_{H_2} is the number of moles of H₂ produced, N_{ph} is the number of incident photons per second and is calculated by equation 2

$$N_{ph} = \frac{I \times A \times \lambda}{ch} \quad (5)$$

Where I is the light intensity, A is the area of the catalyst, λ is the wavelength of the LED, c is the speed of light, and h is the plank constant [38].

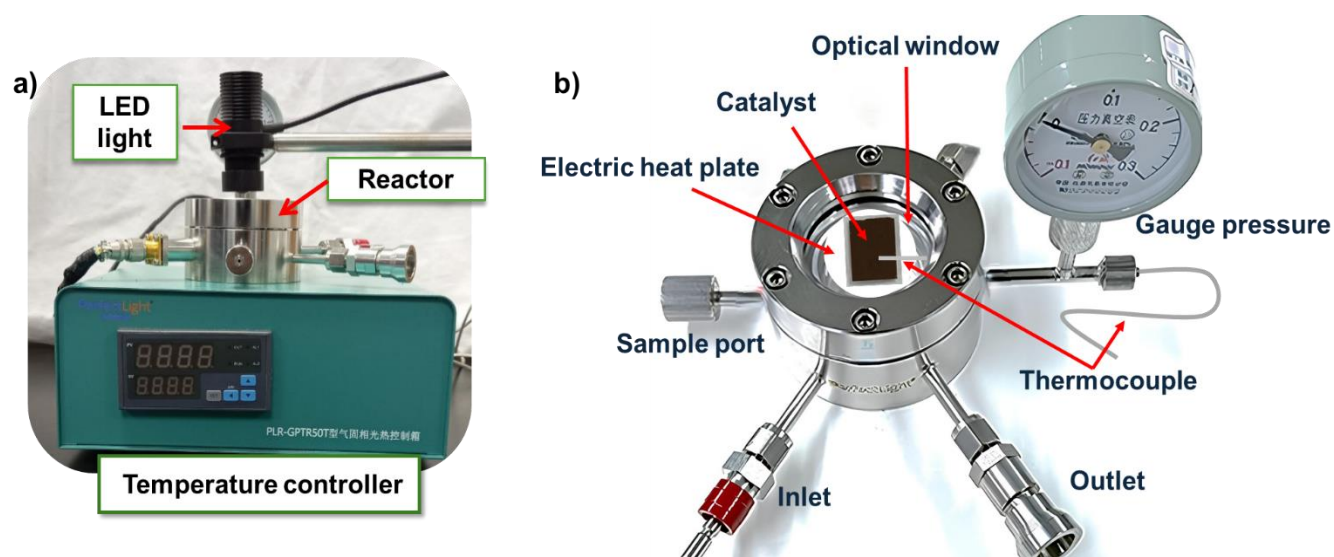


Fig. 2. 2: Photograph of (a) the complete test system and (b) the photothermal reactor.

CHAPTER THREE

RESULTS AND CONCLUSION

3.1 Thermo-photocatalytic MSR over TiO₂ modified with Au nanoparticles

3.1.1 Characterization results

The X-ray diffraction (XRD) pattern of synthesized pristine and Au-modified TiO₂ materials are presented in Fig. 3.1a. It is obvious from Fig. 3.1a that TiO₂ (A-200), either pristine or loaded with 1.0 wt.% Au, exhibits a broader diffraction peak than those of TiO₂ (A-400) and TiO₂ (A-600), which indicates that TiO₂ (A-200) heat-treated at 200 °C is less crystalline. As the calcination temperature increases to 400 and 600 °C, the diffraction peaks become narrow and sharp indicating higher crystallinity. No diffraction pattern associated with Au NPs is observed, suggesting either the Au is highly dispersed, or the Au loading mass is too low to be detected. The XRD diffraction patterns of TiO₂ (Br) and 1.0 wt.% Au/TiO₂ (Br) presented in Fig. 3.1a can be indexed to the reference peaks of brookite phase evincing the successful preparation. The XRD patterns of pristine and Au-modified TiO₂ P25 was also included, and it shows the peaks of rutile and anatase. The TiO₂ materials were further characterized by UV-Vis diffuse reflectance spectra (DRS) and presented in Fig. 3.1 b. Unlike the pristine TiO₂, an absorption peak was observed at around 550 nm in the Au-loaded TiO₂ samples. This peak is related to the surface plasmon resonance of gold nanoparticles. Raman spectroscopy is a versatile technique for ascertaining the structural characteristics and electronic interactions within the Au/TiO₂ (A-200) composite. Fig. 3.1c displays the Raman spectra of the Au/TiO₂ (A-200). All fundamental Raman-active characteristics of anatase are consistently seen in TiO₂ (A-200). However, after the deposition of Au NPs, the shifting of the Raman peaks is observed. While interference in the intensity of the Raman features

caused by the surface plasmon resonance of Au, with incident photons at 633 nm, is anticipated, a shift in Raman features requires electrical contact between TiO₂ (A) and Au NPs. [39]

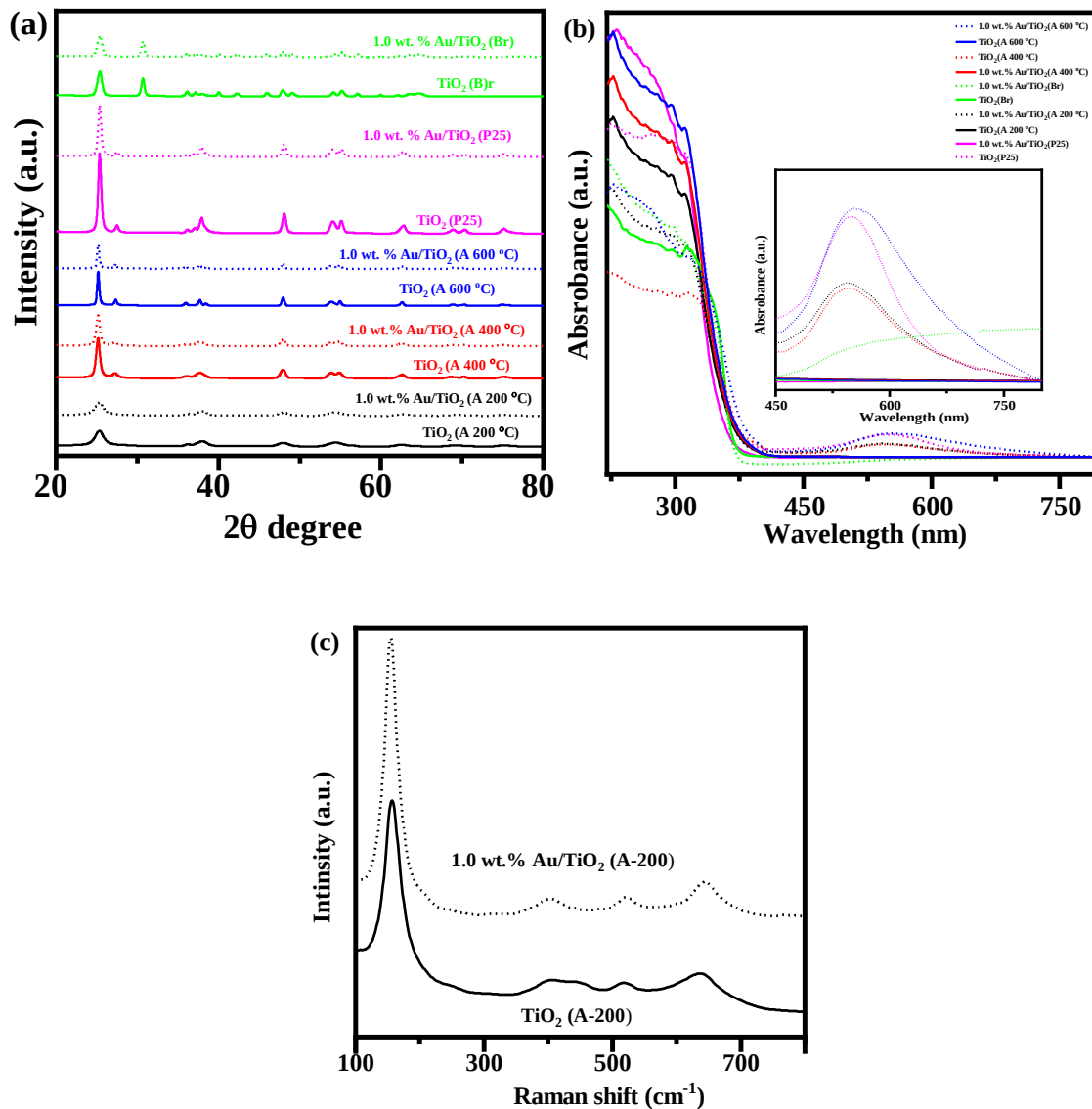


Fig. 3. 1: (a) XRD patterns and (b) DRS of pristine and 1.0 wt.% Au-modified TiO₂ materials, and (c) Raman spectra of TiO₂ (A-200) and 1.0 wt.% Au/TiO₂ (A-200) materials.

The Au loading on the TiO₂ samples were analysed and confirmed by field-emission transmission electron microscopy (FE-TEM). Fig. 3.2a and b shows low and high-resolution TEM images of 1.0 wt.% Au/TiO₂ (P25, Br, A200) indicated that the Au NPs are well dispersed on the surface of TiO₂. It is also observed from the TEM images that TiO₂ (P25) and TiO₂ (Br) Fig. 3.2c and d are more crystalline than TiO₂ (A-200) Fig. 3.2e and f. A HR-TEM image showed a clear lattice fringe of 0.23 nm, consistent with the (111) facet of metallic Au.

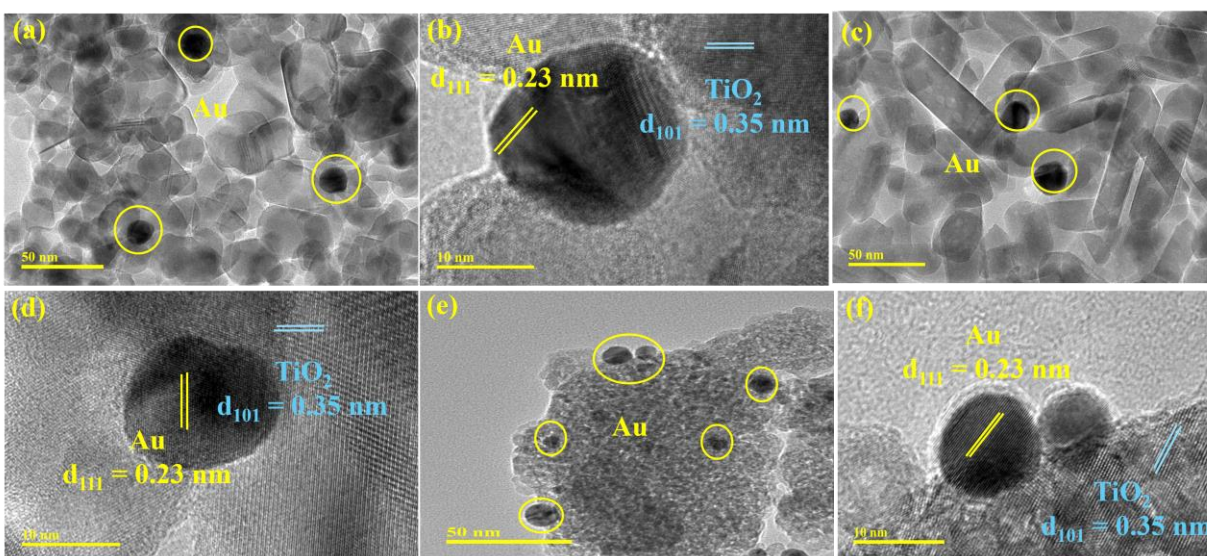


Fig. 3. 2: Low and high-resolution TEM images of (a-b) 1.0 wt.% Au/TiO₂ (P25), (c-d) 1.0 wt.% Au/TiO₂ (Br), and (e-f) 1.0 wt.% Au/TiO₂ (A), respectively, showing the interface between Au and TiO₂.

XPS analysis was conducted to ascertain the composition and identify the chemical states of the pure TiO₂ (A-200) and 1.0 wt.% Au/TiO₂ (A-200). Fig. 3.3. illustrates the high-resolution XPS spectra of Ti 2p, Au 4f, and O 1s in the pure TiO₂ (A-200) and 1.0 wt.% Au/TiO₂ (A-200). The Ti 2p spectra for the TiO₂ (A-200) and 1.0 wt.% Au/TiO₂ (A-200), depicted in Fig. 3.3a, exhibit peaks at 458.6 eV and 464.3 eV in a 2:1 area ratio, which can be attributed to photoemission from the Ti 2p_{3/2} and 2p_{1/2} states of Ti⁴⁺ in TiO₂. [40] However, after adding Au NPs, the Ti 2p peaks are shifted towards lower binding energy due to the interaction with Au. The binding energies of Au

$4f_{7/2}$ and $4f_{5/2}$ for the 1.0 wt.% Au/TiO₂ (A-200) presented in Fig. 3 .3b are located at 82.83 and 86.53 eV, respectively. According to the XPS handbooks and prior reports, the binding energy estimates Au $4f_{7/2}$ for metallic Au were centered at 84.0 eV.[41] Arrii *et al.* investigated the binding energy shift of gold nanoparticles supported on TiO₂. Despite observing a significant shift (up to -1.17 eV for Au/TiO₂ (A-200)), the authors determined that gold remains in the metallic form, as they did not detect any peaks corresponding to oxidized gold species (about 85.5 eV).[42] They ascribed the adverse change to the electron transfer from the support to the Au nanoparticles. According to the report, we assert that in 1.0 wt.% Au/TiO₂ (A-200) gold exists in a metallic state, and the shift of Au $4f_{7/2}$ peak towards lower binding energy suggests a robust interaction between Au particles and the TiO₂ (A-200) support.[43] The O 1s spectrum of pure TiO₂ (A-200) in Fig. 3. 3c is deconvoluted into two peaks: a prominent peak at 529.9 eV corresponding to lattice oxygen (O_L) and a minor peak at 531.02 eV attributed to surface-adsorbed oxygenated species (O_S), such as -OH and H₂O.[44] The O 1s peaks are observed at 530.1 eV for O_L and 531.7 eV for O_S in the context of 1.0 wt.% Au/TiO₂ (A-200).

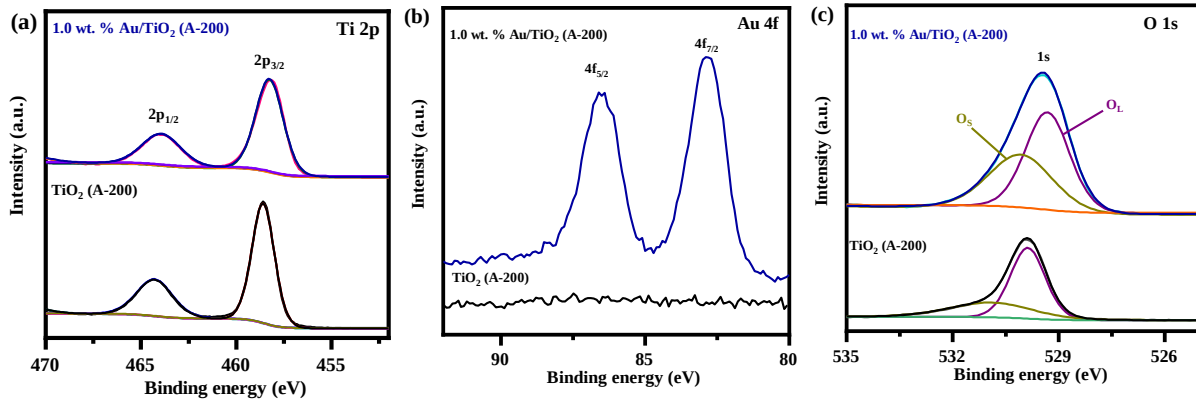


Fig. 3. 3: XPS spectra of (a) Ti 2p, (b) Au 4f, and (c) O 1s of pure TiO₂ (A-200) and 1.0 wt.% Au/TiO₂ (A-200).

3.1.2 Thermo-photocatalytic MSR

The thermo-photocatalytic (TPC) methanol steam reforming (MSR) experiments were performed in a stainless-steel reactor. The reactor chamber contains a thermocouple in intimate contact with the catalyst bed, which was used to monitor the surface temperature. Fig. 3.4 (a-c) shows the H₂ and CO₂ production rate via MSR over 1.0 wt.% Au/TiO₂ (P25, Br, and A-200) at 100 °C under 25.0 mW cm⁻¹ 365 nm irradiance. We also measured these catalysts' H₂ and CO₂ formation rates through MSR at 150 °C under the same illumination conditions presented in Fig 3.5(a-c). It is observed from Fig. 3.4 (a-c) that there is no complete reforming of methanol into H₂ and CO₂ due to the formation of CO [45]. But, as shown from Fig 3.5 (a-c), complete MSR with H₂-to-CO₂ ratio of three could be achieved at 150 °C.

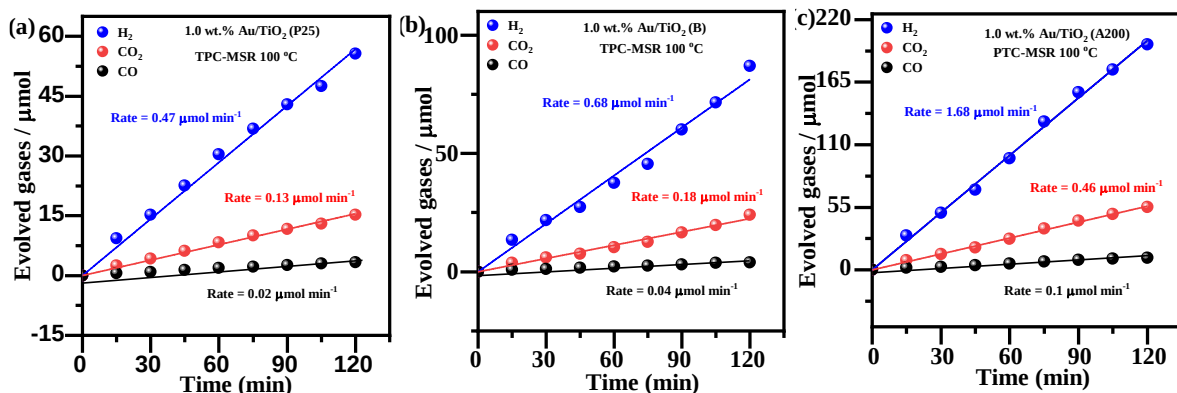


Fig. 3. 4: The amount of H₂, CO and CO₂ produced via TPC-MSR over (a) 1.0 wt.% Au/TiO₂ (P25), (b) 1.0 wt.% Au/TiO₂ (Br), and (c) 1.0 wt.% Au/TiO₂ (A-200), respectively at 100 °C.

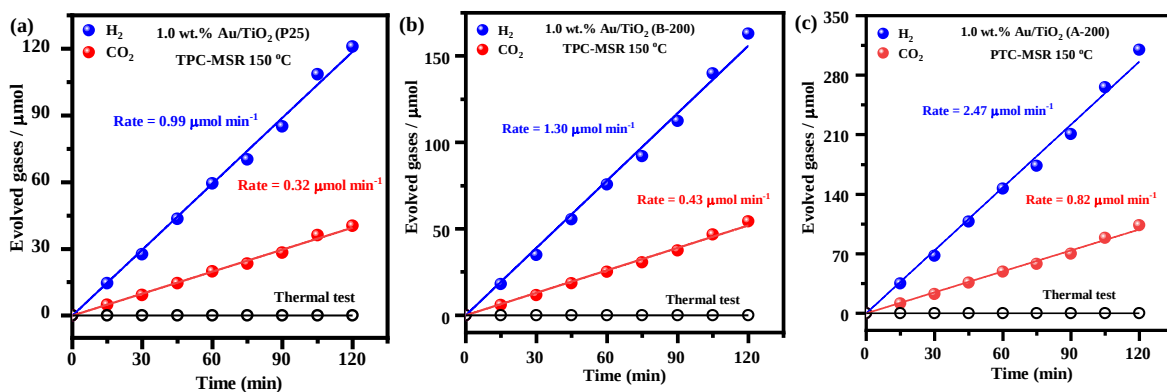


Fig. 3. 5: The amount of H₂, CO and CO₂ produced via TPC-MSR over (a) 1.0 wt.% Au/TiO₂ (P25), (b) 1.0 wt.% Au/TiO₂ (Br), and (c) 1.0 wt.% Au/TiO₂ (A-200), respectively at 150 °C.

Fig. 3.6 shows the rates H₂ and CO₂ production over 1.0 wt.% Au TiO₂ (P25, A, and Br) and bare TiO₂ (A200), which were calcined at 200 °C. It is observed from Fig. 3.6 that out of all thermo-photocatalysts mentioned above, 1.0 wt.% Au/TiO₂ (A-200) could achieve the highest rate of 370 mmol g⁻¹ h⁻¹ W⁻¹ with the complete MSR at 150 °C under 25mW cm⁻¹ 365 nm irradiance [46].

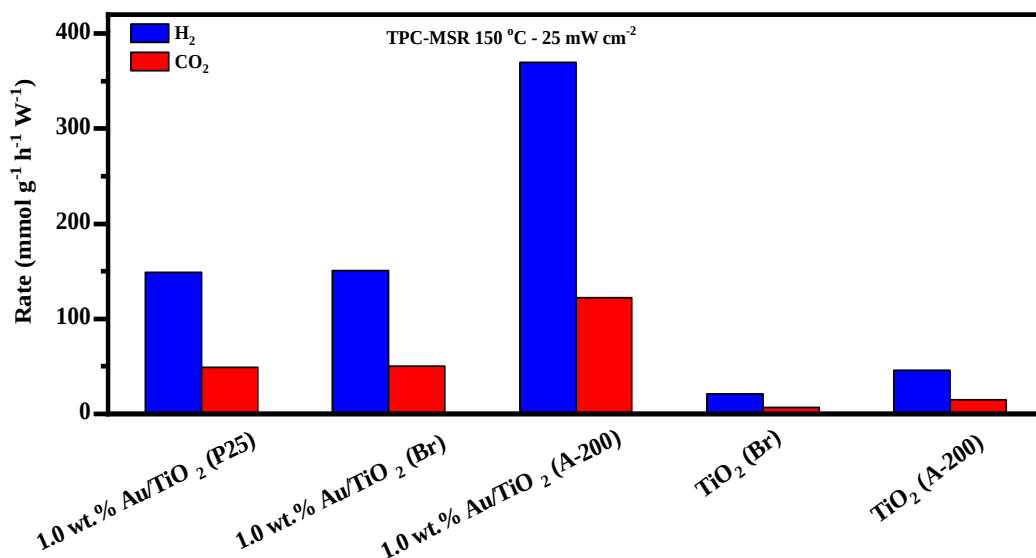


Fig. 3. 6: Rate of H₂ and CO₂ production over different thermo-photocatalysts via MSR at 150 °C.

The main reason for the high activity of 1.0 wt.% Au/TiO₂ (A-200) was attributed to its high BET surface area. This has been confirmed by comparing the hydrogen production rate with the crystallite size and BET surface area at different calcination temperatures (Fig. 3.7) [46].

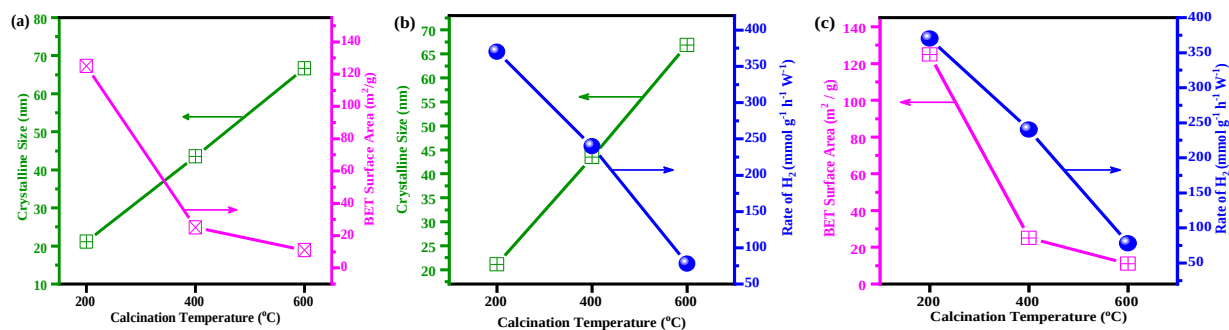


Fig. 3. 7: The effect of calcination temperature on (a) crystallite size and BET surface area, (b) crystallite size and rate of hydrogen evolution, and (c) BET surface area surface area and rate of hydrogen evolution over 1.0 wt.% Au/TiO₂ (A-200).

Fig. 3.8a shows the effect of light intensity of LED 365 nm on the amount of H₂ produced during the TPC-MSR over 1.0 wt.% Au/TiO₂ (A-200) catalyst at 150 °C. It is observed from Fig. 3.8a that as the LED light intensity increases, there is an exponential enhancement in the MSR rate (amount of H₂ produced) due to the enhancement in the number of photons passing through the given area at a particular time [47]. Fig. 3.8b compares the TPC-MSR and TC-MSR performance of 1.0 wt.% Au/TiO₂ (A-200) under light (365 nm LED, 25 mW) and in the dark at various temperatures (150, 200, and 250 °C). As seen from Fig. 3.8b, 1.0 wt.% Au/TiO₂ (A-200) catalyst is thermally inactive at low temperatures, but as the temperature is enhanced to 200 °C, small H₂ and CO₂ formation peaks are observed [48]. Under light illumination (365 nm LED, 25 mW), there is a significant amount of H₂ and CO₂ produced, which increases with increasing temperature from 150-250 °C. To understand and explore the role of the gold (Au) nanoparticles deposited on TiO₂ (A-200), the TPC-MSR process was performed at two different monochromatic light LEDs (365 and 560 nm) of 25 mW intensity at 150 °C and compared with DRS results Fig. 3.8c [49]. It is

observed from Fig. 3.8c that there is a good match between the apparent quantum efficiency and the DRS confirming the hot-carriers contribution to the MSR process. Under light illuminations electrons would go from the conduction band of TiO_2 (A) to Au NPs, which inhibited the recombination of charge carriers and significantly enhances the MSR process [50].

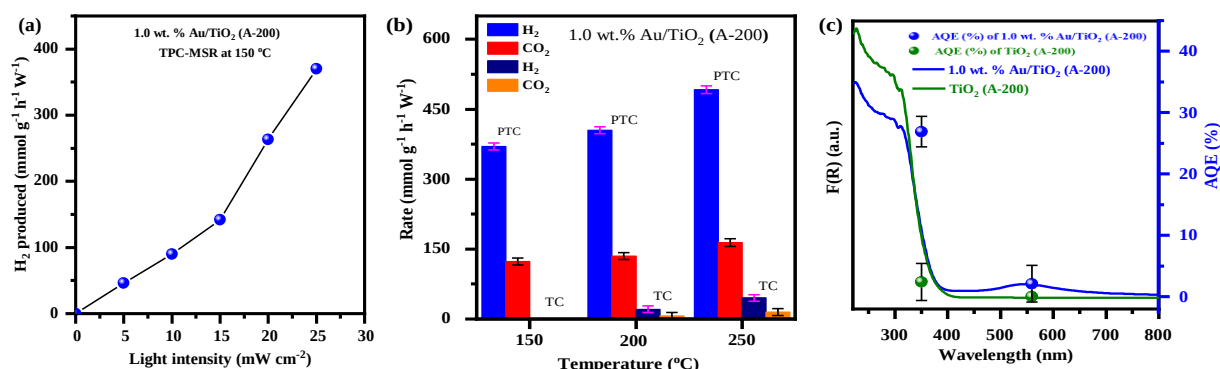


Fig. 3. 8: (a) Effect of light intensity on the amount of H_2 produced by TPC-MSR over 1.0 wt.% Au/TiO₂ (A-200), (b) photothermal (TPC) and thermal (T) MSR over 1.0 wt.% Au/TiO₂ (A-200) at different temperatures, and (c) The action spectrum of 1.0 wt.% Au/TiO₂ (A-200).

At the given temperature range, the TPC-MSR H_2 generation rates were markedly superior to those achieved through thermal catalysis, demonstrating a photo-driven augmentation of MSR at these temperatures [51]. The hydrogen production rates for MSR driven by light were significantly higher compared to those achieved through thermal catalysis at the same temperature, highlighting the enhancement of MSR under photo-driven conditions. As shown in the Arrhenius plots presented in Fig. 3.9a the apparent activation energy for MSR over 1.0 wt.% Au/TiO₂ (A-200) decreased markedly from $95.14 \text{ kJ mol}^{-1}$ under dark (thermocatalytic) conditions to only $25.46 \text{ kJ mol}^{-1}$ under UV-Vis illumination.[52, 53]. In addition to its remarkable TPC activity, 1.0 wt.% Au/TiO₂ (A-200) exhibits excellent stability. Fig. 3.9b shows no noticeable decrease in the activity for TPC hydrogen production by MSR for 11 hours. Therefore, the remarkable activity and stability make 1.0 wt. % Au/TiO₂ (A-200) a promising semiconductor thermo-photocatalytic for MSR.

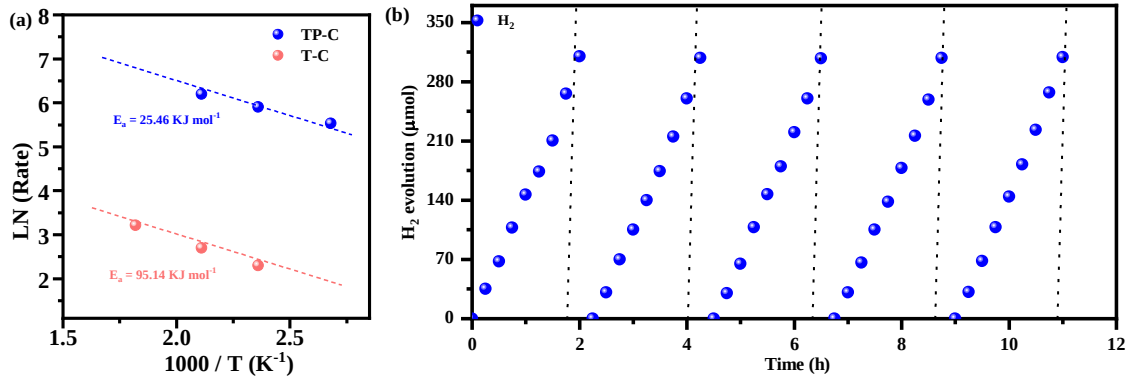


Fig. 3. 9: (a) Arrhenius plot for TPC H₂ production over 1.0 wt.% Au/TiO₂ (A-200) and (b) Stability test of 1.0 wt. % Au/TiO₂ (A-200) under TPC-MSR (each cycle was kept for 120 min).

3.1.3 Mechanisms of TPC MSR over Au/TiO₂ catalyst.

Reaction pathways for thermo-photocatalytic methanol steam reforming (TPC-MSR) on 1.0 wt. % Au/TiO₂ (A-200) involves the following steps: (i) photogeneration of electron and hole pairs, (ii) adsorbed species on the surface of photocatalyst react with separated charge carriers: i.e., adsorbed H₂O and CH₃OH are oxidized by holes with the formation of [•]OH and various fragments including CH₃O[•], CH₂O[•], CHO[•], HCOO[•], and HCOOH. (iii) as-formed HCOOH is further oxidized to CO₂. (iv) the proton formed is reduced by the electrons either on the CB of TiO₂ or by the trapped electrons by Au to form H₂ [54]. The initial steps for the methanol oxidation are illustrated in Fig. 3.10 and the follow reforming steps are summarized in Eqs. 6-9.



The methanol and water in the system act as a scavenger for photo-generated holes on the VB of TiO_2 . The products, including H_2 and CO_2 , were detected by GC. The loading of the Au nanoparticles on the surface of TiO_2 not only facilitated the separation of photogenerated charge carriers but also provided more reactive sites for hydrogen evolution, resulting in the enhanced TPC activity.[25] Pure TiO_2 shows a small amount at H_2 ($35 \text{ mmol g}^{-1} \text{ h}^{-1} \text{ W}^{-1}$) compared to modified 1.0 wt.% Au/TiO_2 (A-200) ($370 \text{ mmol g}^{-1} \text{ h}^{-1} \text{ W}^{-1}$).

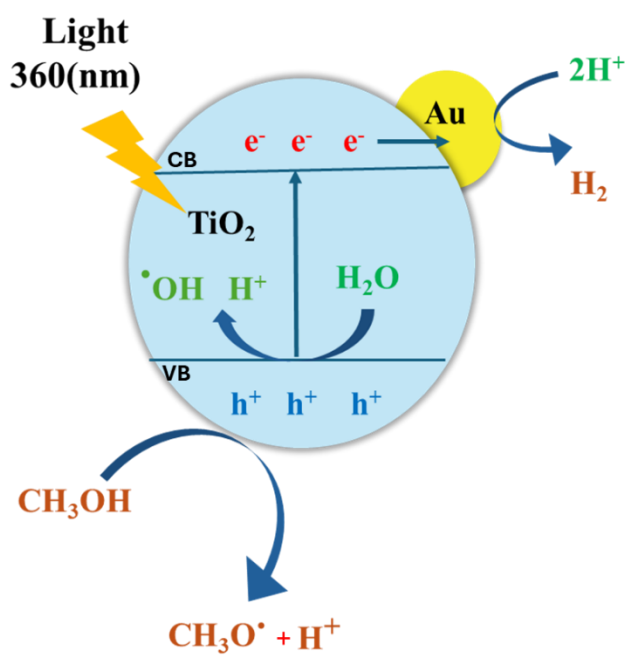


Fig. 3. 10: Schematic representation of the PT-MSR of 1.0 wt. % Au/TiO_2 (A-200) catalyst.

3.2 Plasmonic Photothermal (PTC) MSR over $\text{TiO}_2@\text{Cu}/\text{Al}_2\text{O}_3$

3.2.1 Characterization results

The $\text{R-Cu}/\text{Al}_2\text{O}_3$ and $\text{TiO}_2@\text{R-Cu}/\text{Al}_2\text{O}_3$ plasmonic photothermal catalysts were synthesized by reducing the CuAl-LDH and CuAl-LDH modified with TiO_2 P25 (either by physical mixing or in-situ adding method, see experimental section) in an H_2/Ar (10/90 v/v) environment at 300 °C. The crystal structure of the as-prepared (i.e. CuAl-LDH and $\text{TiO}_2@\text{CuAl-LDH}$) and the reduced (i.e. $\text{R-Cu}/\text{Al}_2\text{O}_3$ and $\text{TiO}_2@\text{R-Cu}/\text{Al}_2\text{O}_3$) materials were studied by X-ray diffraction (XRD). Fig. 3.11a shows the XRD patterns of TiO_2 P25, CuAl-LDH , and CuAl-LDH physically mixed with different amounts of TiO_2 P25 (i.e. 0.5, 1.0, 2.5, 5, 10, 50 wt%). The commercial TiO_2 P25 consists of a mixture of anatase (ca. 80%) and rutile (ca. 20%) according to the manufacturer's technical report and the diffraction peaks of anatase and rutile can be readily indexed. At 1.0 wt% loading of TiO_2 on the CuAl-LDH , the XRD diffraction peaks of TiO_2 were not detected evincing good mixing with the CuAl-LDH . As the amount of TiO_2 P25 increased to 2.5 wt%, the TiO_2 most intense peak of (101) facet at $2\theta = 25^\circ$ can be detected. Fig 3.11b showed the XRD patterns of the $\text{TiO}_2@\text{CuAl-LDH}$ materials obtained by the in-situ adding TiO_2 P25 during the synthesis of CuAl-LDH . It is observed from Fig. 3.11b that the in-situ addition of TiO_2 P25 changes the XRD pattern

of the CuAl-LDH and leads to CuO_x formation. This indicated that the in-situ addition of TiO_2 P25 suppressed the formation of the CuAl-LDH structure.

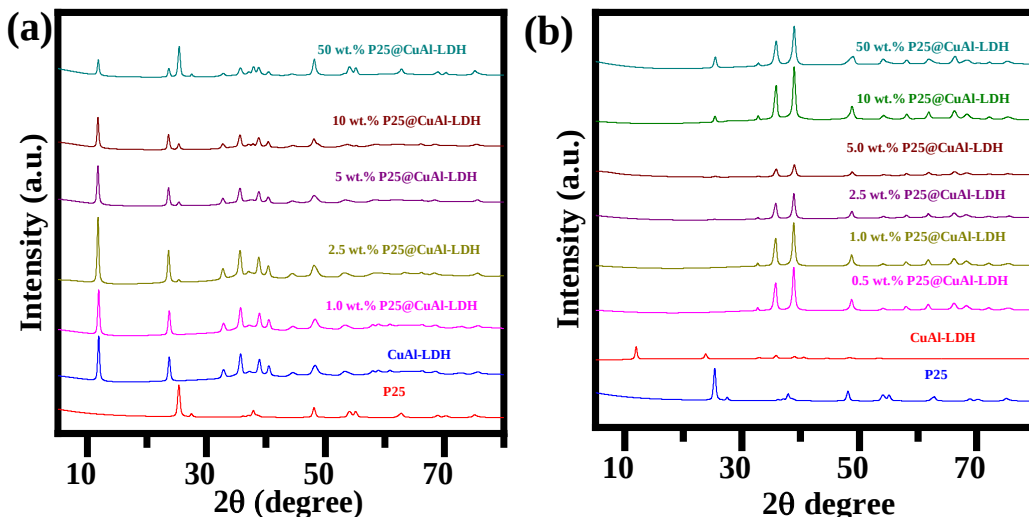


Fig. 3. 11: XRD patterns of TiO_2 P25, CuAl-LDH, and CuAl-LDH modified with different amounts of TiO_2 P25 using (a) physical mixing and (b) in-situ adding.

For ease of comparison, Fig. 3.12a shows the XRD patterns of TiO_2 P25, CuAl-LDH, 1.0 wt% TiO_2 -PM@CuAl-LDH (physically mixed), and 1.0 wt% TiO_2 -IA@R-Cu/ Al_2O_3 (in-situ added) catalysts. The XRD patterns of CuAl-LDH and 1.0 wt% TiO_2 -PM@CuAl-LDH showed the LDH characteristic diffraction peaks of (003), (006), and (012) facets located at $2\theta = 11.8^\circ$, 23.7° , and 32.8° , respectively [54]. After reduction with H_2 at 300°C , the LDH structure of the CuAl-LDH and 1.0 wt% TiO_2 -PM@CuAl-LDH collapsed, and new diffraction peaks at different 2θ appeared due to the formation of metallic Cu nanoparticles according to JCPDS # 04-0836 see Fig. 3.12b. No Al_2O_3 -related XRD peaks have been seen after the reduction indicating that Al_2O_3 exist in an

amorphous phase. However, the in-situ addition of TiO_2 prevents the formation of LDH structure, still, the reduction of 1.0 wt% $\text{TiO}_2\text{-IA@CuAl-LDH}$ leads to the formation of Cu metal

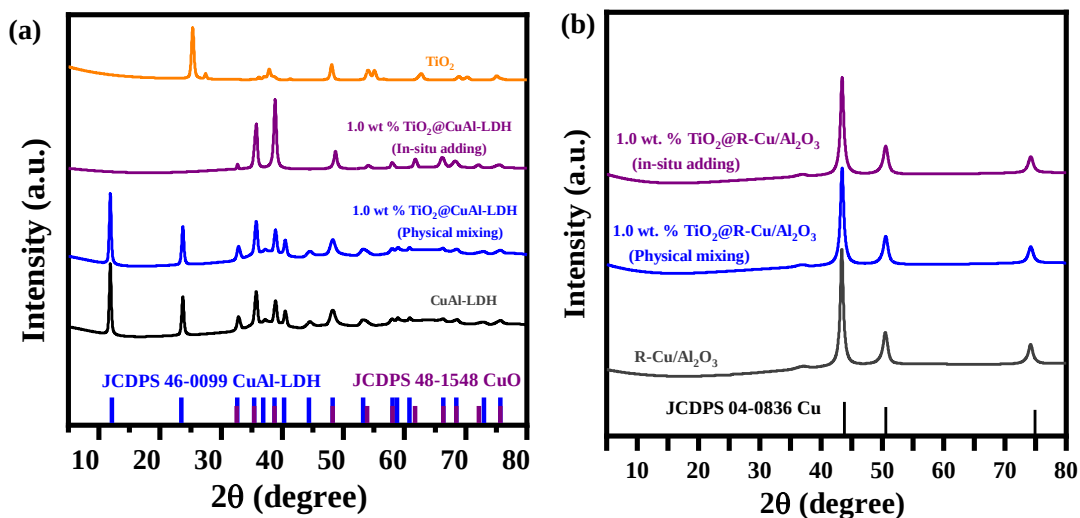


Fig. 3. 12: XRD patterns of (a) as-prepared CuAl-LDH, 1.0 wt% $\text{TiO}_2\text{-PM@CuAl-LDH}$ (physical mixing) and 1.0 wt% $\text{TiO}_2\text{-IA@CuAl-LDH}$ (in-situ adding); and (b) R-Cu/ Al_2O_3 , 1.0 wt % $\text{TiO}_2\text{-PM@R-Cu/Al}_2\text{O}_3$, and 1.0 wt % $\text{TiO}_2\text{-IA@R-Cu/Al}_2\text{O}_3$ after reduction.

Transmission electron microscopy (TEM) was used to study morphologies of CuAl-LDH, 1.0 wt.% $\text{TiO}_2\text{@R-Cu/Al}_2\text{O}_3$ (physically mixed), R-Cu/ Al_2O_3 , and 1.0 wt.% $\text{TiO}_2\text{@R-Cu/Al}_2\text{O}_3$ catalysts. Fig. 3.13 (a & c) shows the low-resolution TEM images of CuAl-LDH and 1.0 wt.% $\text{TiO}_2\text{@CuAl-LDH}$. It is observed from these images that CuAl-LDH has a typical layered 2D structure containing nanoparticles of TiO_2 P25 in 1.0 wt.% $\text{TiO}_2\text{@CuAl-LDH}$ Fig. 3.13c. Fig. 3.13 (b & d) shows the high-resolution TEM images CuAl-LDH and 1.0 wt.% $\text{TiO}_2\text{@CuAl-LDH}$. The CuAl-LDH lattice fringes were observed with an interplanar distance of 0.24 nm corresponding to the (002) facet.[55] The lattice spacing of 0.34 nm could be indexed to the (101) reflection of TiO_2 . [56] The layered structure of LDH is destroyed after reduction, R-Cu/ Al_2O_3 and 1.0 wt.% $\text{TiO}_2\text{@R-Cu/Al}_2\text{O}_3$ catalysts consist of metallic copper and TiO_2 nanoparticles supported on

alumina Fig. 3.13 (e-h). The high-resolution TEM images in Fig. 3.13 (f & h) showed lattice fringes with a spacing of 0.20 nm and 0.34 nm, corresponding to metallic Cu (111) and TiO_2 (101) planes.[23]

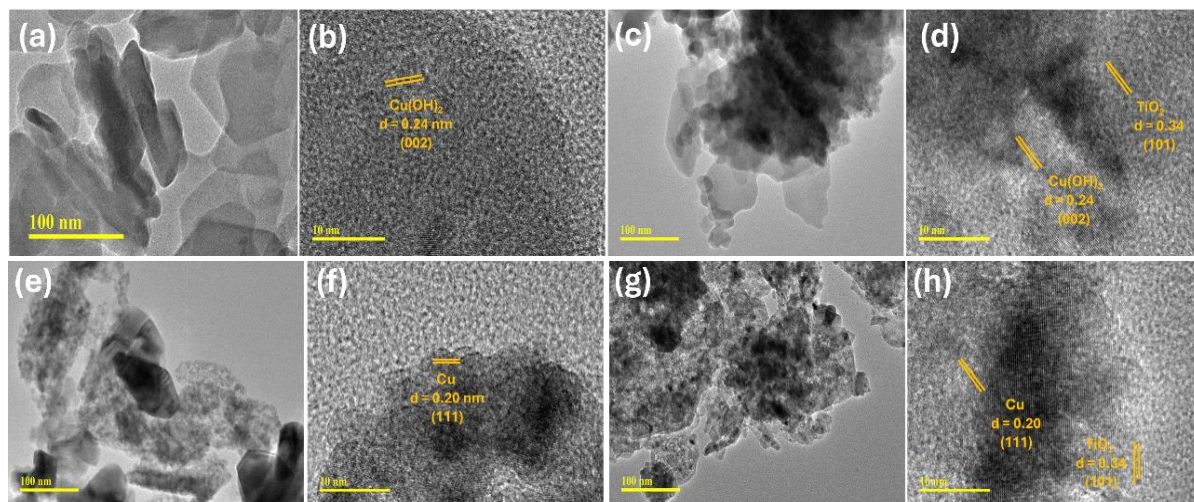


Fig. 3. 13: Low and high-resolution TEM images of (a & b) CuAl-LDH, (c & d) 1.0 wt.% TiO_2 @CuAl-LDH, (e & f) R-Cu/ Al_2O_3 , and (g & h) 1.0 wt.% TiO_2 @R-Cu/ Al_2O_3 catalysts, respectively.

XPS analysis was carried out to investigate the surface chemical composition and valence states of Cu, Al, and Ti of CuAl-LDH and 1.0 wt.% TiO_2 PM@CuAl-LDH before and after reduction. The Cu 2p spectra of CuAl-LDH and 1.0 wt.% TiO_2 PM@CuAl-LDH before and after reduction are presented in Fig 3.14a and Fig 3.15a. It is observed from Fig. 3.14a that the CuAl-LDH and 1.0 wt.% TiO_2 PM@CuAl-LDH before reduction contained two satellite peaks with Cu $2p_{3/2}$ and Cu $2p_{1/2}$ peaks; these satellites indicated that Cu is present in the +2-oxidation state. After the reduction (R-Cu/ Al_2O_3 and 1.0 wt.% TiO_2 @R-Cu/ Al_2O_3), the absence of these satellites indicated that metallic Cu was the dominant copper species in R-Cu/ Al_2O_3 and 1.0 wt.% TiO_2 @R-Cu/ Al_2O_3 . [57] The Al 2p XPS spectra of CuAl-LDH and 1.0 wt.% TiO_2 PM@CuAl-LDH presented in Fig. 3.14b and Fig 3.15b indicated that Al is present in $\text{Al}(\text{OH})_3$, while after reduction (R-Cu/ Al_2O_3 and 1.0 wt% TiO_2 PM@R-Cu/ Al_2O_3), Al is present in the form of Al_2O_3 . [58, 59]

Figs. 3.14c and 3.15c shows the XPS spectra of Ti 2p of 1.0 wt.% TiO_2 PM@CuAl-LDH before and after reduction. It is also observed from these figures that there is no change in the peak position of Ti 2p before and after the reduction, indicating that TiO_2 is not reduced.

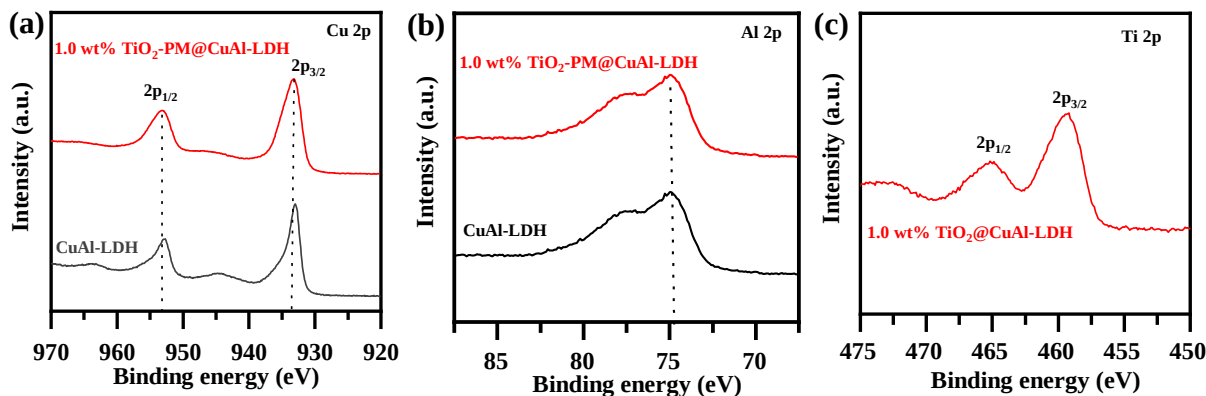


Fig. 3. 14: High-resolution XPS spectra of Cu 2p (a), Al 2p (b), and Ti 2p (c) in CuAl-LDH and 1.0 wt.% TiO_2 -PM@CuAl-LDH before reduction.

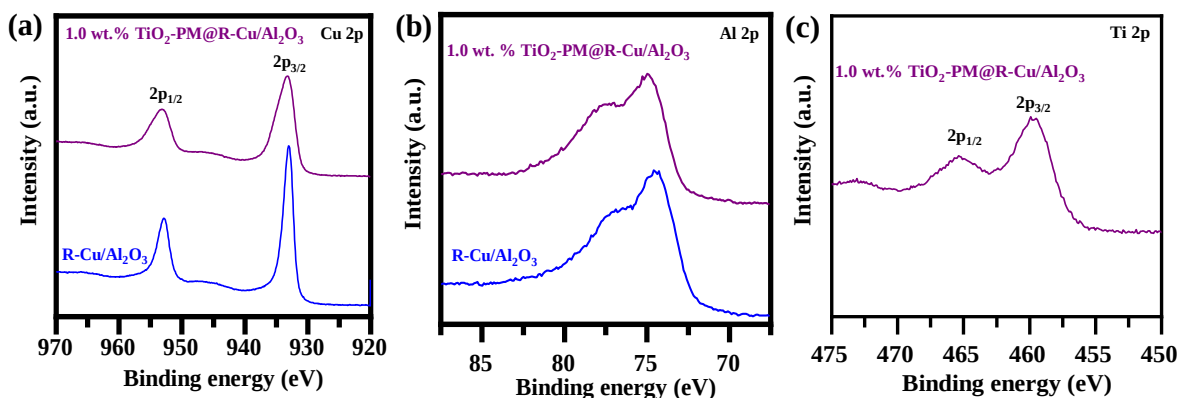


Fig. 3. 15: High-resolution XPS spectra of Cu 2p (a), Al 2p (b), and Ti 2p (c) in CuAl-LDH and 1.0 wt.% TiO_2 -PM@CuAl-LDH after reduction.

Fig. 3.16a shows the diffuse reflectance spectra (DRS) of CuAl-LDH and 1.0 wt.% TiO_2 -PM@CuAl-LDH before and after reduction. The reduced samples (R-Cu/ Al_2O_3 and 1.0 wt.% TiO_2 -PM@R-Cu/ Al_2O_3) showed a broad absorption peak covering almost the entire visible light range up to 780 nm. This broad peak is attributed to the localized surface plasmon resonance (LSPR) of the metallic Cu.

Fig 16b presents the FT-IR spectra of the CuAl-LDH, R-Cu/Al₂O₃, 1.0 wt% TiO₂-PM@CuAl-LDH, and 1.0 wt% TiO₂-PM@R-Cu/Al₂O₃. The intense broad band observed in CuAl-LDH and 1.0 wt% TiO₂-PM@CuAl-LDH at 3409 cm⁻¹ is attributed to the O–H stretching vibration, whereas the weak peak located at 1566 cm⁻¹ is attributed to the bending vibrations of hydroxyl groups and the interlayer water molecules.[60, 61] The sharp peak located at 1360 cm⁻¹ is due CO₃²⁻ ions .[62] These O–H stretching, bending, and CO₃²⁻ ions vibrations peaks disappeared in the reduced forms (R-Cu/Al₂O₃ and 1.0 wt% TiO₂-PM@R-Cu/Al₂O₃) due to the decomposition of the CuAl-LDH and the formation of Cu nanoparticles supported on Al₂O₃.

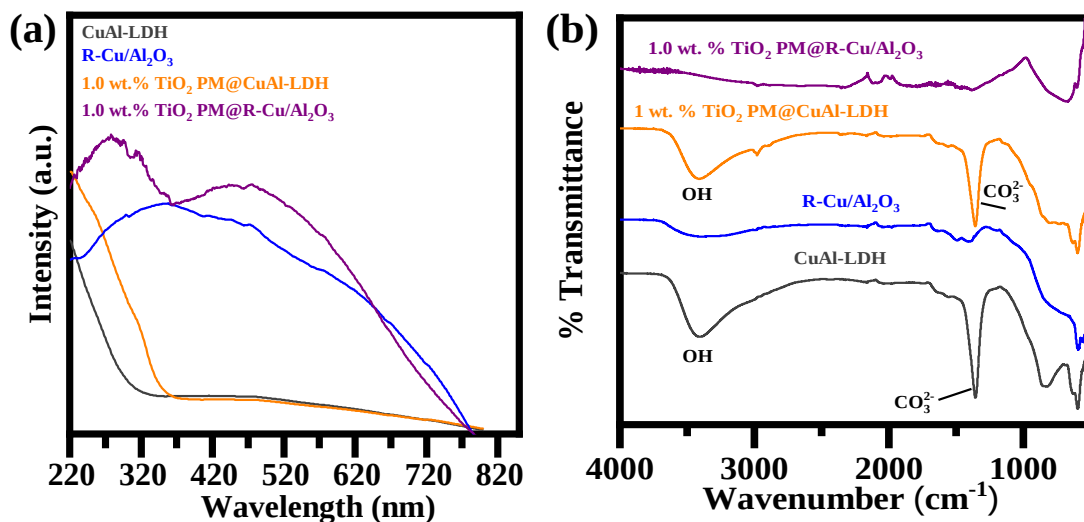


Fig. 3. 16: (a) DRS and (b) FT-IR spectra of CuAl-LDH, R-Cu/Al₂O₃, 1.0 wt.% TiO₂ PM@CuAl-LDH, and 1.0 wt.% TiO₂@R-Cu/Al₂O₃ catalysts, respectively.

3.2.2 Photothermal MSR

The time course of evolved H₂ and CO₂ via PTC-MSR over R-Cu/Al₂O₃ and 1.0 wt% TiO₂-PM@R-Cu/Al₂O₃ catalysts at 200 °C was measured and is presented in Fig 3.17a. As a reference, the rates of thermocatalytic H₂ and CO₂ evolution over the R-Cu/Al₂O₃ catalyst are presented in Fig. 3.18. It can be seen that the light (1.0 sun, AM1.5G) has improved the rate of hydrogen

production over R-Cu/Al₂O₃ from 8.9 to 37.0 mmol g⁻¹ h⁻¹, that is by more than 4-fold. For comparison of all PTC catalysts, the light normalized rates of H₂ and CO₂ evolution were calculated and are shown in Fig 3.17b. As illustrated in Fig 3.17b, the R-Cu/Al₂O₃ catalyst modified with 1.0 wt% TiO₂ by physical mixing exhibits the highest activity. Pristine TiO₂ exhibits negligible H₂ and CO₂ production rates. Interestingly, the rate of PTC hydrogen evolution over R-Cu/Al₂O₃ (i.e. 92 mmol g⁻¹ h⁻¹ W⁻¹) is enhanced by 66% after the modification with 1.0 wt% TiO₂ by a facile physical mixing method and reached 153 mmol g⁻¹ h⁻¹ W⁻¹. The in-situ addition of TiO₂ during the synthesis of CuAl-LDH was investigated. This approach resulted also in a significant improvement (48%) in activity but did not reach the rate achieved by the physical mixing method. As discussed earlier, the in-situ addition of TiO₂ suppresses the formation of CuAl-LDH structures, leading instead to the formation of CuO_x. This indicates that the CuAl-LDH structure is crucial for achieving a catalyst with optimal activity, more likely, due to the better dispersion of the Cu nanoparticles on the Al₂O₃ support formed after the reduction.

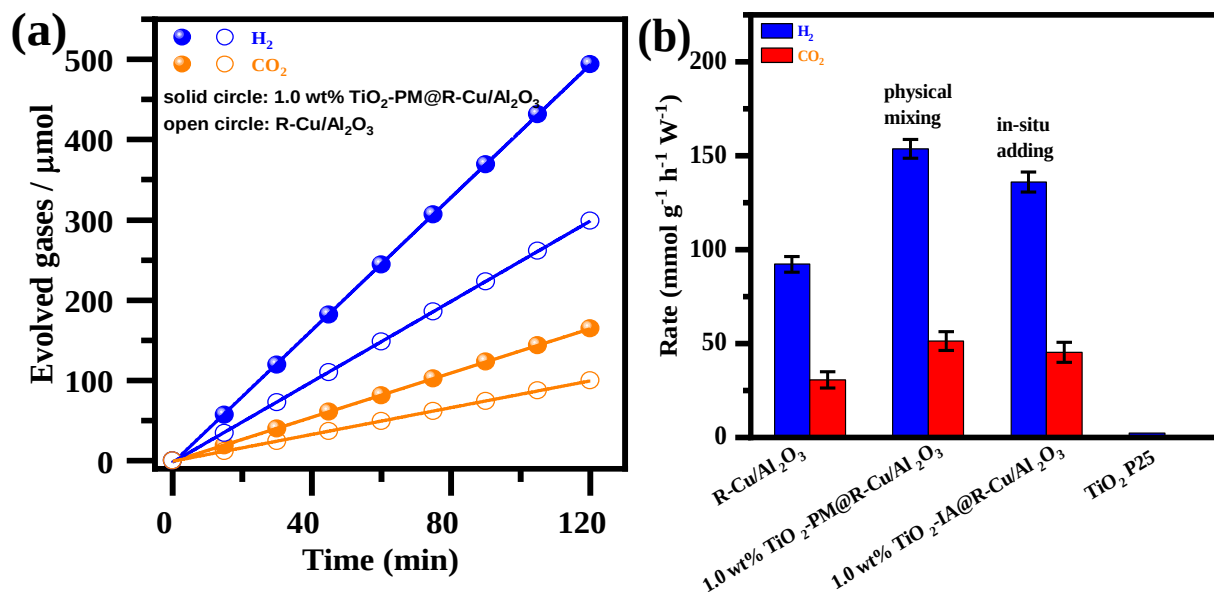


Fig. 3. 17: (a) Time course of PTC H₂ and CO₂ production via MSR over R-Cu/Al₂O₃ and 1.0 wt% TiO₂-PM@R-Cu/Al₂O₃ catalysts at a temperature of 200 °C and 1.0 sun illumination, and (b) Comparison of the normalized rates for H₂ and CO₂ production over investigated catalysts at same conditions.

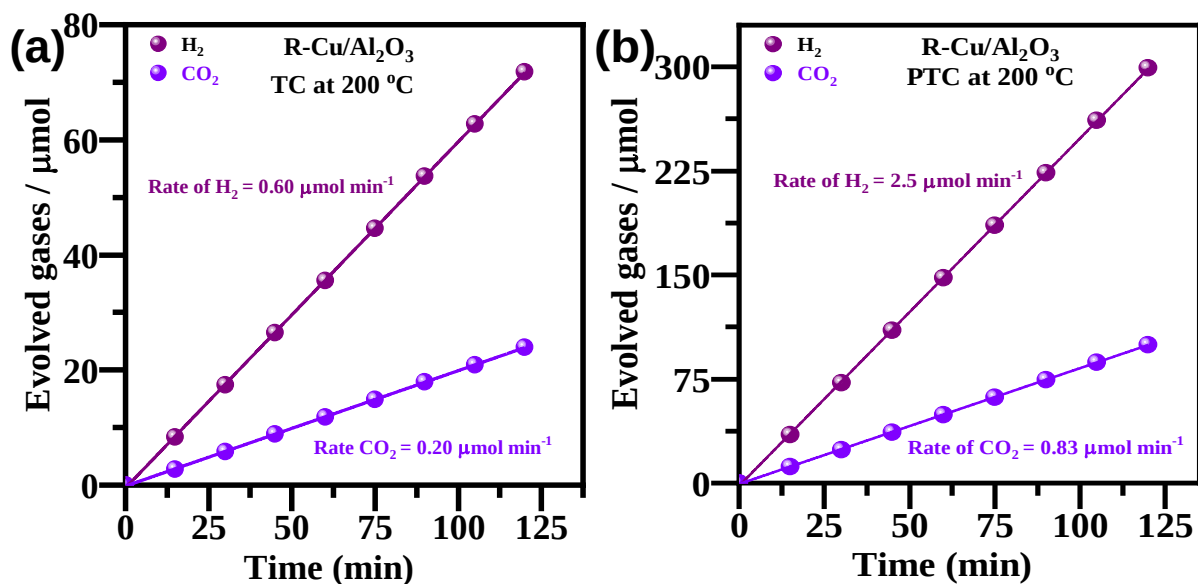


Fig. 3. 18: Time course of H₂ and CO₂ evolution by thermocatalytic (a) and photothermal catalytic (b) MSR over R-Cu/Al₂O₃ at 200 °C.

To explore the thermocatalytic (TC) contribution, the H₂ and CO₂ evolution via MSR over the 1.0 wt% TiO₂-PM@R-Cu/Al₂O₃ catalyst was studied at different temperatures (150, 200, and 250 °C) in the absence of light. The results are presented in Figs. 3.19a, b, and c. For comparison, the time courses of the PTC H₂ and CO₂ evolution under 1.0 sun illumination were also recorded (Fig. 3.20a, b, and c). It is worth mentioning that the temperature sensor was placed close to the catalyst surface, ensuring that the temperature remained constant in both the presence and absence of light.

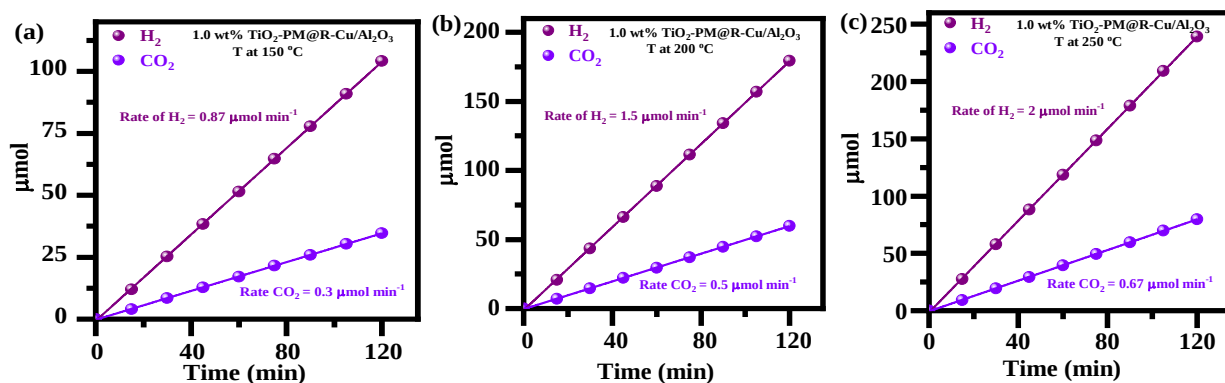


Fig. 3. 19: Time course of H_2 and CO_2 evolution by thermal catalytic MSR over 1.0 wt% TiO_2 -PM@R-Cu/ Al_2O_3 at (a) 150, (b) 200, and (c) 250 °C.

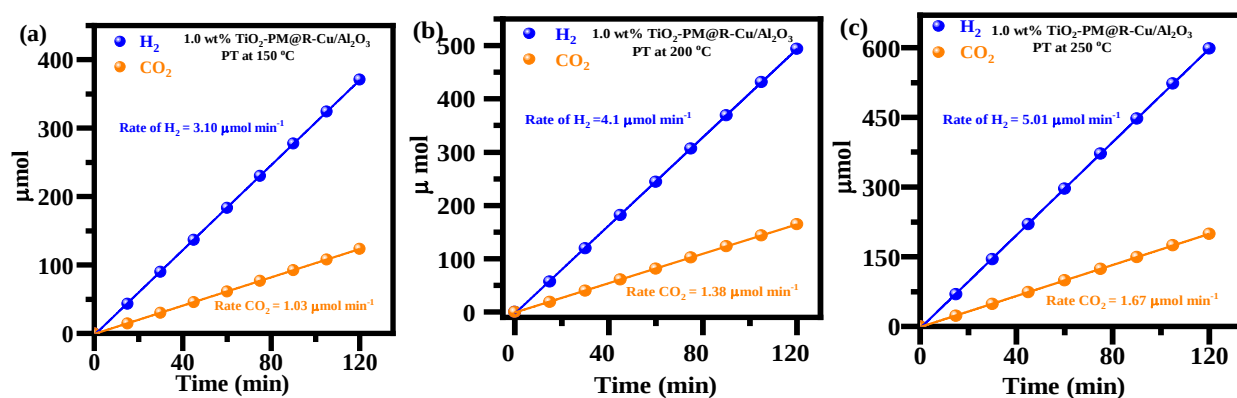


Fig. 3. 20: Time course of H_2 and CO_2 evolution by photothermal catalytic MSR over 1.0 wt% TiO_2 -PM@R-Cu/ Al_2O_3 at (a) 150, (b) 200, and (c) 250 °C.

The normalized H_2 and CO_2 production rates ($mmol g^{-1} h^{-1}$) were calculated and are shown in Fig. 3.21a and b. A significant improvement in activity was observed under light at all temperatures, indicating that light positively impacts the MSR process and likely initiates photo-induced reactions. Specifically, the ratios of the rate of H_2 production via PTC-MSR to that of TC-MSR were 3.5, 2.7, and 2.5 at 150, 200, and 250 °C, respectively. The observed decrease in the enhancement ratio due to the light effect with increasing temperature can be attributed to the

suppressed plasmonic effect at higher temperatures and/or due to the enhanced kinetics of thermocatalytic reactions [63].

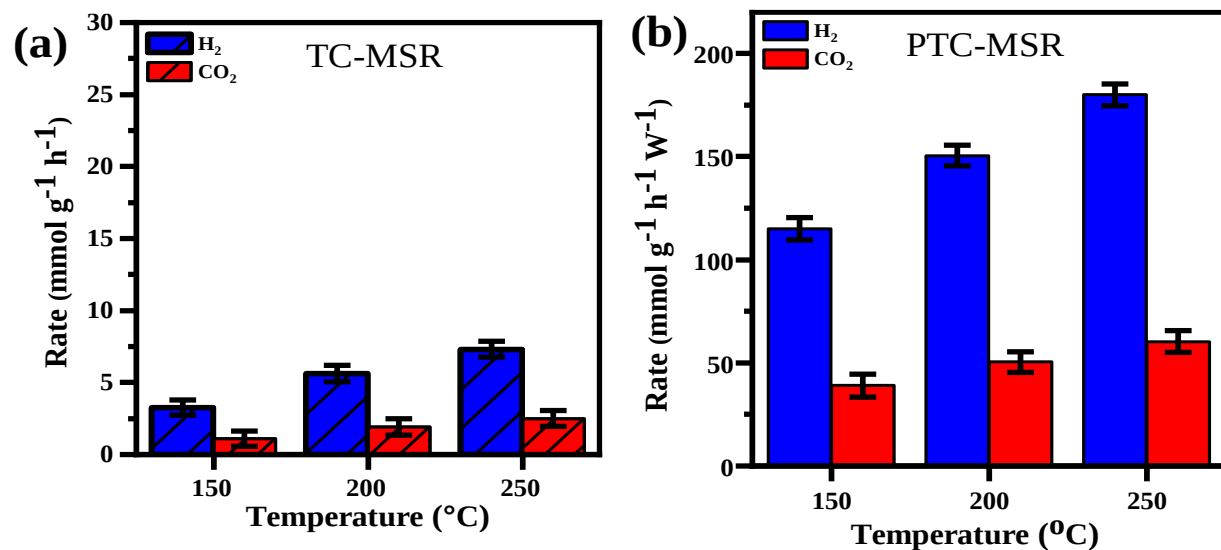


Fig. 3. 21: Normalized rate of H₂ and CO₂ production via MSR over 1.0 wt% TiO₂-PM@R-Cu/Al₂O₃ catalyst at different temperatures (a) TC-MSR and (b) PTC-MSR under 1.0 sun illumination.

In general, the main objective of using the plasmonic catalyst is to improve the MSR output per unit of light energy input, whether through thermal or non-thermal approaches. To evaluate that, the overall light effectiveness (OLE) index in plasmonic catalysis was recently proposed and it can be calculated using Eq. (10)[63].

$$\text{OLE } (\mu\text{mol s}^{-1}/\text{W} \times \text{cm}^{-2}) = \frac{\text{Total production rate enhanced by light } (\mu\text{mol s}^{-1})}{\text{Light intensity } (\text{W} \times \text{cm}^{-2})} \quad (10)$$

The OLE compares the amount of additional products produced via PTC-SMR compared with TC-MSR conditions, per second per unit power of light, regardless of catalytic mass. The OLE values of the most active 1.0 wt% TiO₂-PM@R-Cu/Al₂O₃ catalyst were found to be 0.37, 0.43, and 0.50 $\mu\text{mol s}^{-1}/\text{W cm}^{-2}$ at 150, 200, and 250 °C, respectively, concerning the hydrogen production. These

values again indicate that the light has a significant impact at all investigated temperatures on the rate of hydrogen production via MSR.

As presented earlier, we found that the physical mixing of 1.0 wt% of TiO_2 with the CuAl-LDH resulted in a significant improvement in the hydrogen production rate (i.e. from a rate of 92.0 to 153 $\text{mmol g}^{-1} \text{h}^{-1} \text{W}^{-1}$). Fig. 3.22a shows the influence of the amount of TiO_2 (0.5, 1.0, 2.5, 5.0, 7.5, 10.0, and 50.0 wt%) on the PTC-SMR reactions (Note: TiO_2 was physically mixed with CuAl-LDH and then reduced in a hydrogen environment, see experimental section). It is observed from Fig. 3.22a that 1.0 wt% TiO_2 is enough to promote the PTC-MSR process. At 1.0 wt% TiO_2 loading, H_2 and CO_2 production rates of 153 and 51 $\text{mmol g}^{-1} \text{h}^{-1} \text{W}^{-1}$ were achieved, respectively [23].

At higher TiO_2 loading, the PTC-MSR rate started to decline gradually more likely due to shielding the Cu active sites with TiO_2 and also due to shielding the light since TiO_2 absorbs the UV light only, while the plasmonic Cu absorbs the entire visible light range see Fig. 3.22b. The influence of TiO_2 loading using the in-situ addition during the synthesis of CuAl-LDH was also tested. As shown in Fig. 3.22b, the 1.0 wt% TiO_2 is sufficient to improve the PTC-SMR, but the rate is significantly decreased with increasing the amount of TiO_2 . In addition to the shielding effect, this rapid decrease in the activity associated with the formation of CuO_x instead of CuAl-LDH as

revealed from the XRD data presented in Fig. 3.9a. This indicates that the use of CuAl-LDH as a precursor for the R-Cu/Al₂O₃ is crucial for the improved PTC-MSR reaction.

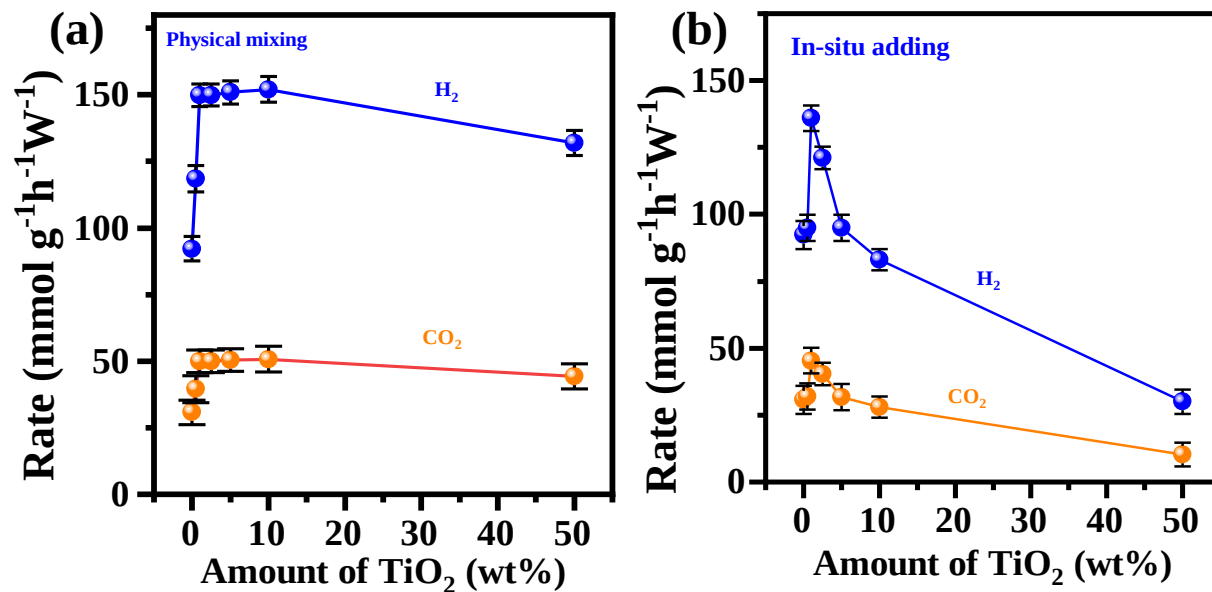


Fig. 3. 19: (a) Influence of the amount of TiO₂ loaded by (a) physical mixing and (b) in-situ adding on the H₂ and CO₂ production via the PTC-MSR.

Theoretically, the catalytic production of H_2 by SMR reaction can be expressed by Eq. (11):



According to Eq. 2, at complete reforming of methanol, the expected mole ratio of H_2 to CO_2 should be 3.0. This ratio is achieved at all temperatures, indicating that the 1.0 wt.% TiO_2 -PM@R-Cu/ Al_2O_3 is a promising photothermal catalyst for the MSR application. No CO has been detected and CO-Free hydron can be achieved after the separation of CO_2 . To ensure the visible light activity of the 1.0 wt.% TiO_2 @R-Cu/ Al_2O_3 , the rate of hydrogen production via PTC-MSR hydrogen at different monochromatic light was calculated, and the action spectrum was constructed and presented in Fig. 3.23a. It is observed that the rate of H_2 production closely followed the localized surface plasmon resonance (LSPR) spectrum of Cu nanoparticles in the 1.0 wt.% TiO_2 @R-Cu/ Al_2O_3 catalyst. This verifies that the LSPR excitation of the Cu nanoparticles contributed to the enhanced photothermal activity of the catalyst under solar light irradiation. Subsequent stability studies were performed (three consecutive cycles), with no catalytic deactivation observed Fig. 3.23b.

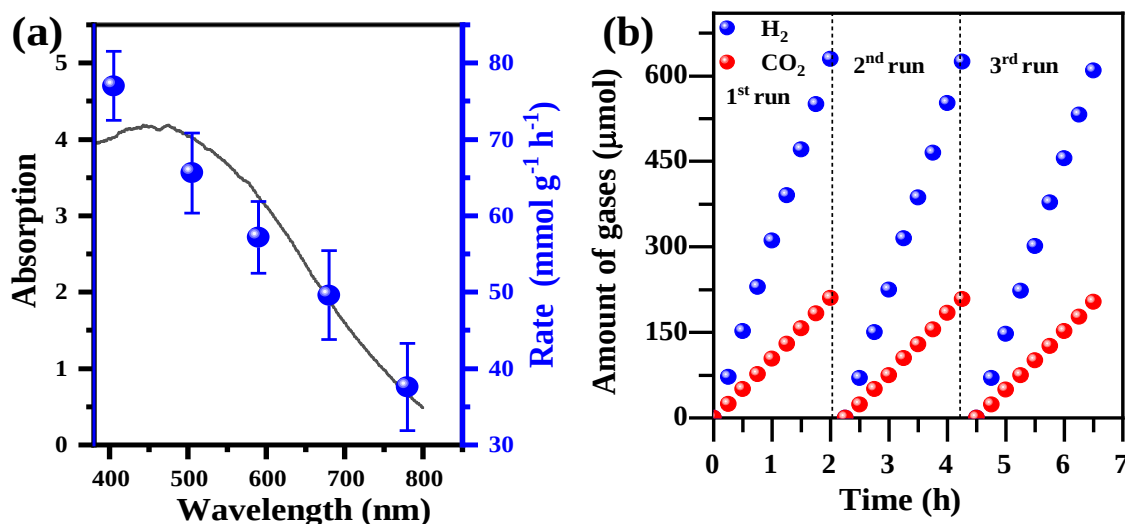


Fig. 3. 20: (a) Action spectrum and (b) stability test for H_2 and CO_2 evolution via PTC-MSR over 1.0 wt% TiO_2 -PM@R-Cu/ Al_2O_3 catalyst.

3.2.3 Mechanism of photothermal MSR process

As presented in Fig. 3.17b TiO₂ P25 has negligible activity compared to the 1.0 wt% TiO₂-PM@R-Cu/Al₂O₃ catalyst. This indicates that TiO₂ P25 neither contributes to the TC-MSR nor to the PTC-MSR processes. The action spectrum presented in Fig. 3.23a confirmed the visible light response of the 1.0 wt% TiO₂-PM@R-Cu/Al₂O₃ catalyst. This response matches the DRS spectra of the LSPR of Cu nanoparticles and indicates that Cu nanoparticles are light-active materials. The work function of copper (Cu) typically ranges between 4.5–4.7 eV depending on the crystal face (e.g., Cu(111), Cu(100), or Cu(110)) and it matches the work function of TiO₂ (4.6–5.3 eV) [64]. Thus, the injection of electrons from the conduction band (CB) of Cu to the CB of TiO₂ is possible. Based on those findings the mechanisms of the PTC-MSR over the 1.0 wt% TiO₂-PM@R-Cu/Al₂O₃ catalyst are proposed and presented in Fig. 3.24a. This figure shows the proposed hot carrier-driven PTC-MSR reaction mechanism on the 1.0 wt% TiO₂@R-Cu/Al₂O₃ catalyst. Under solar light illumination, the electrons in the 3d orbitals of Cu NPs supported on Al₂O₃ are excited to high energy levels, generating hot electrons. These high-energy hot electrons can be injected quickly into the CB of TiO₂. The Schottky junction at the TiO₂/Cu interface could trap the transferred hot electrons and delay them from transferring back to Cu NPs under continuous visible light irradiation. Thus, the electron-rich sites can be formed at the interface between Cu and TiO₂. At the same time, the surface electronic state of Cu NPs is positively charged due to electronic depletion, leading to the formation of electron-deficient Cu^{δ+} sites at the Cu surface. The electron-rich sites at the TiO₂/Cu interface mediate the reduction of H⁺ to H^{*} species and the formation of H₂. At the same time, for the electron-deficient counterpart, Cu^{δ+} sites are more liable to accept σ electrons of CH₃OH and H₂O and facilitated C–H and O–H bond cleavage to yield ^{*}CH₂OH and

OH^{*} species, and subsequently, CO₂ through the formation of HCHO and HCOOH as proposed by Takezawa and Iwasa for the copper-based catalysts [65, 66].

It is known that the TiO₂ surface has a low activity for hydrogen evolution reactions, and it can store electrons for a long time [67]. It is usually modified with a noble metal co-catalyst as active sites for hydrogen production. Thus, to further support the plausible hot-electron transfer from the Cu to TiO₂, the TiO₂ was modified with 1.0 wt% Au before being physically mixed with the CuAl-LDH using the same amount (1.0 wt%). Then the sample was treated the same way as for 1.0 wt% TiO₂@R-Cu/Al₂O₃. If the electrons are transferred from the Cu to the CB of TiO₂, the modification of TiO₂ with an Au should improve the rate of hydrogen evolution. Indeed, as shown in Fig. 3.24c, the rate of PTC-MSR hydrogen production was improved after modifying TiO₂ with Au. The electrons would transfer from the Cu to the CB of TiO₂ where they transfer to Au nanoparticles, which act as active centers for the hydrogen evolution and suppress recombination.

In our study, the H₂ to CO₂ ratio was three, and no CO gas has been detected. Based on that and the above discussion, the proposed reaction steps for the PTC-MSR process are summarized in Eqs. 12- 18 as follows [67]:



In the same manner, the HCHO and HCOOH can be oxidized.





In fact, the formation of the photon-induced hot-electrons and $\text{Cu}^{\delta+}$ sites facilitate the PTC-MSR process by minimizing the activation energy relative to that of the TC-MSR as evinced from the Arrhenius plot presented in (Fig. 3.b).

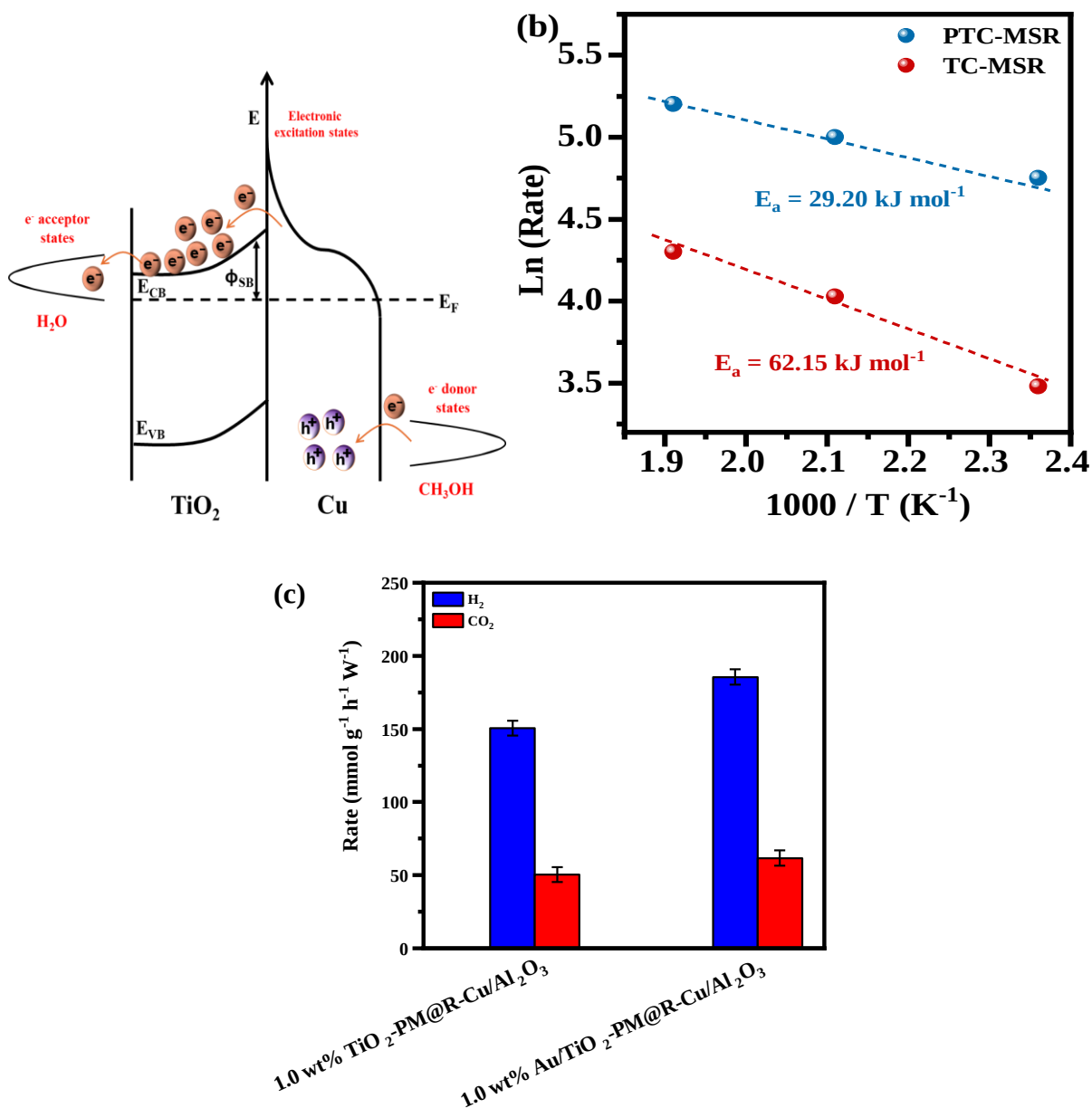


Fig. 3. 21: (a) Illustration for the proposed role of TiO_2 in the hot carrier-enhanced PTC-MSR over $1.0 \text{ wt\% TiO}_2\text{-PM@R-Cu/Al}_2\text{O}_3$ catalyst and (b) Apparent activation energy for the TC-MSR and PTC-MSR processes and (c) Influence of the modification of TiO_2 with Au on the rate of hydrogen evolution via PTC-MSR process.

CHAPTER FOUR

CONCLUSION & FUTURE RECOMMENDATIONS

4.1 Conclusion

This study highlights the remarkable potential of thermo-photo catalysis for methanol steam reforming (MSR) as a sustainable approach to hydrogen transport and production. By integrating plasmonic nanoparticles with TiO₂ nanomaterials, we demonstrated significant improvements in the catalytic MSR process at a low temperature. The anatase TiO₂ modified with 1.0 wt.% Au nanoparticles achieved an exceptional thermo-photocatalytic hydrogen production rate 370.0 mmol g⁻¹ h⁻¹ W⁻¹ under UV light at 150 °C, far exceeding the performance of conventional thermal-only catalysts. This illustrates the critical role of light in reducing the activation energy, thereby reducing the reaction temperature and boosting hydrogen yield.

Furthermore, plasmonic Cu nanoparticles supported on Al₂O₃ were successfully derived from CuAl-LDH by reduction under a hydrogen atmosphere at 300 °C (R-Cu/Al₂O₃). It absorbs the solar light up to 780 nm and showed a 4-fold higher plasmonic photothermal catalytic (PTC) hydrogen production rate via methanol MSR than that of the thermocatalytic (TC) under 1.0 sun illumination at 200 °C. Interestingly, the modification of the R-Cu/Al₂O₃ with 1.0 wt% TiO₂ using a facile physical mixing method was sufficient to improve the PTC hydrogen production rate from 92.0 to 153 mmol g⁻¹ h⁻¹ W⁻¹ resulting in an improvement by 66 %. Moreover, the methanol was completely reformed with H₂ to CO₂ ratio equal three and no CO gas has been detected. The improved PTC activity upon the modification with small amount of TiO₂ was attributed to the synergy between TiO₂ and the LSPR of Cu nanoparticles. Under solar light illumination, the electrons in the 3d orbitals of Cu NPs are excited to high energy levels, generating hot electrons.

These high-energy hot electrons are quickly injected into the CB of TiO₂. At the same time, the surface electronic state of Cu NPs is positively charged due to electronic depletion, leading to the formation of electron-deficient Cu^{δ+} sites. The presence of TiO₂ facilitates the separation of these photo-induced reactive species and thus improves the PTC-MSR activity. The photo-induced reactive species reduced the activation energy to half and thus improved the kinetics of the PTC-MSR relative to the TC-MSR.

4.2 Future work

- Test the PTC-MSR in a continuous flow reactor (at high pressure, industrial relevant conditions) and estimate the conversion efficiency.
- Test these approaches for other substrates including CO₂ hydrogenation and methane reforming.

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Vitae

Name :Mohammed Altigani Aldaw Abdalmwla |
Nationality :Sudanese |
Date of Birth :11/11/1996|
Email :m.altigani114@gmail.com|
Address :Al_Managil, Al_Jazirah, Khartoum, Sudan. |

Academic Background

1. MSc in Chemistry (Material Chemistry), 2024
King Fahad University of Petroleum and Minerals.
2. B.Sc. in Chemistry, 2020
University of Khartoum, Khartoum, Sudan.

PUBLICATIONS:

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