KIV- Buku Profile ✓

Status ✓ 25/11

Universiti Malaysia PAHANG

RESEARCH REPORT UMP GRANT

Laporan Prestasi Skim Geran UMP

Final	/	Progress		*Progress Period :*	*√ Please tick*

PROJECT DETAILS *(Keterangan Projek)*

A		
	Grant No	RDU1603137 ✓ Ext. date : 4/11/2019 (ERAS)
	Faculty/CoE	FACULTY OF CIVIL ENGINEERING TECHNOLOGY
	Project Title	DEVELOPMENT AND MODIFICATION OF TIO2 BASED-NANOPHOTOCATALYST FOR DIRECT CONVERSION OF CO2 TO HYDROCARBON FUEL
	Project Leader	DR. AZRINA ABD AZIZ
	Project Member	1. PROF. MADYA DR. CHE KU MOHAMMAD FAIZAL BIN CHE KU YAHYA 2. DR. MUZAMIR HASAN (CERRM) 3. PROF. DR. SHALIZA IBRAHIM (UNIVERSITY OF MALAYA)

PROJECT ACHIEVEMENT *(Pencapaian Projek)*

B

ACHIEVEMENT PERCENTAGE				
Project progress according to milestones achieved up to this period	**0 - 25%**	**26 - 50%**	**51 - 75%**	**76 - 100%**
Percentage (please state %)				**100%** ✓

EXPENDITURE *(Perbelanjaan)*

C

Budget Approved *Peruntukan diluluskan*	**Amount Spent** *Jumlah Perbelanjaan*	**Balance** *Baki*	**% of Amount Spent** *Peratusan Belanja*
RM 29000	**RM 27903**	**RM 1097**	**96.2%** ✓

RESEARCH OUTPUT *(Output Penyelidikan)*

D

NO OF PUBLICATION

KPI FOR NO OF PUBLICATION

	ISI	Scopus	Index Proceedings	Others
KPI	1	1	1	
Achievement	1 ✓	1 ✓	1 ✓	

The contribution of funder (UMP, MOHE, MOSTI, Industry etc.) as the fund provider must be acknowledged at all times in all forms of publications. Please state the grant number (RDU/UIC) and grant name.

	ISI	Scopus
Number of articles/ manuscripts/books *(Please attach the First Page of Publication)*	1. MECHANISTIC INSIGHTS INTO PLASMONIC PHOTOCATALYSTS IN UTILIZING VISIBLE LIGHT	1. PREPARATION OF ACTIVATED CARBON/N-DOPED TITANIA COMPOSITE FOR SYNERGISTIC ADSORPTION PHOTOCATALYTIC OXIDATION OF BATIK DYE

KPI Achievement:
1 MSC
1 ISI + Acknowledgement
1 Scopus + Acknowledgement
1 Index Proceeding

	International	National
Conference Proceeding *(Please attach the First Page of Publication)*	1. **PREPARATION OF ACTIVATED CARBON/ N-DOPED TITANIA COMPOSITE FOR SYNERGISTIC ADSORPTION-PHOTOCATALYTIC OXIDATION OF BATIK DYE.**	1. 2.

HUMAN CAPITAL DEVELOPMENT

KPI FOR HUMAN CAPITAL DEVELOPMENT

	PhD Student	Master Student
KPI		1
Achievement		1

Human Capital Development	**Number**				**Others** (please specify)
	On-going		**Graduated**		
Citizen	Malaysian	Non Malaysian	Malaysian	Non Malaysian	
PhD Student					
Masters Student		1 ✓			
Undergraduate Student					
Total		1			

Name of Student:
FATEMA KHATUN
ID Matric No: MET17005
Faculty: FTKA
Thesis title:
Graduation Year:

Name of Student:
ID Matric No:
Faculty:
Thesis title:
Graduation Year:
*** enter for more space*

INTELECTUAL PROPERTIES

KPI FOR INTELECTUAL PROPERTIES
Patent, Copyright, Trademark,Industrial Design: 0

Patent, Copyright, Trademark, Industrial Design ect	

OTHERS

KPI FOR OTHERS
Prototype, Technology,Collaborations etc: 0

Prototype, Technology, Collaborations etc	

ASSET *(Aset)*

E

Bil	**Peralatan** *(Equipment)*	**Model**	**No Daftar Aset** *(Asset Tagging No)*	**Amount** (RM)	**Lokasi** *(Location)*

PRODUCT DESCRIPTION FOR UMP R&D DIRECTORY (SHORT & BRIEF) *Only for Final Report*

F	**A visible light effective photocatalyst as well as low charge-recombination rate were prepared (RGO-Au/TNTs). The semiconductor TiO2 nanotubes (TNTs) were coupled with noble metal (Gold (Au)) and Reduced Graphene Oxide (RGO) which considered as supporting non-metal.**

PRODUCT PICTURE FOR UMP R&D DIRECTORY *Only for Final Report*

G	**A visible light effective photocatalyst as well as low charge-recombination rate were prepared (RGO-Au/TNTs). The semiconductor TiO2 nanotubes (TNTs) were coupled with noble metal (Gold (Au)) and Reduced Graphene Oxide (RGO) which considered as supporting non-metal.**

SUMMARY OF RESEARCH FINDINGS (*Ringkasan Penemuan Projek Penyelidikan)*

H	**TIO2 BASED-NANOPHOTOCATALYST FOR DIRECT CONVERSION OF CO2 TO HYDROCARBON FUEL**

PROBLEMS / CONSTRAINTS IF ANY *(Masalah/ Kekangan sekiranya ada)*

I	**None**

Date : 7/11/2019
Tarikh

Project Leader's Signature:
Tandatangan Ketua Projek

COMMENTS, IF ANY/ ENDORSEMENT BY FACULTY (*Komen, sekiranya ada / Pengesahan oleh Fakulti*)

J Recommend / ~~Not Recommend / KIV / Need Ammendment~~

.....

.....

.....

Name:
Nama:

Date:
Tarikh: 12.11.19

** Dean/TDR/Director/Deputy Director

Signature:
Tandatangan

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COMMENTS, IF ANY/ ENDORSEMENT BY RMC PNI (*Komen, sekiranya ada / Pengesahan oleh RMC PNI*)

K ~~Recommend / Not Recommend / KIV / Need Ammendment~~

Book profit and final report missing

~~Recommend~~ accepted

KPI achieved

Name:
Nama:

Date:
Tarikh: 17/12/19

Signature:
Tandatangan:

PROFESOR DR. MD. MUSTAFIZUR RAHMAN
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BEILSTEIN JOURNAL OF NANOTECHNOLOGY

Mechanistic insights into plasmonic photocatalysts in utilizing visible light

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Review

Open Access

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Keywords:
localized surface plasmon resonance (LSPR); noble metal; plasmonic photocatalyst; reactive radicals; Schottky junctions; visible light

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Abstract

The utilisation of sunlight as an abundant and renewable resource has motivated the development of sustainable photocatalysts that can collectively harvest visible light. However, the bottleneck in utilising the low energy photons has led to the discovery of plasmonic photocatalysts. The presence of noble metal on the plasmonic photocatalyst enables the harvesting of visible light through the unique characteristic features of the noble metal nanomaterials. Moreover, the formation of interfaces between noble metal particles and semiconductor materials further results in the formation of a Schottky junction. Thereby, the plasmonic characteristics have opened up a new direction in promoting an alternative path that can be of value to the society through sustainable development derived through energy available for all for diverse applications. We have comprehensively prepared this review to specifically focus on fundamental insights into plasmonic photocatalysts, various synthesis routes, together with their strengths and weaknesses, and the interaction of the plasmonic photocatalyst with pollutants as well as the role of active radical generation and identification. The review ends with a pinnacle insight into future perspectives regarding realistic applications of plasmonic photocatalysts.

applications [163]. A very recent study demonstrated that Ag/AgCl can be synthesized using ash gourd peel extract without using organic toxic solvents [157]. Bovine serum albumin (BSA) and Neem extract were used to prepare Ag-ZnO nanostructures, in which both green extracts acted as a shape controllers and reducing agents of Ag^+ to overcome the self-nucleation problem of Ag NPs [164,165].

Direct photocatalysis by plasmonic metals

Plasmonic catalyst systems have almost exclusively focused on the coupling of plasmonic metals (Au and Ag) with semiconductors. Recent reports found that plasmonic metals can be utilised to motivate direct photocatalysis where both light harvesting and activation of reactants take place on the plasmonic metals. It is observed that, unlike semiconductors, the photocatalytic quantum efficiency on plasmonic metal enhances the light intensity and thermal energy absorption. This result shows that plasmonic metals are effective at coupling thermal and photonic stimuli for driving chemical transformations [166]. The rapid recombination of plasmon charge carriers restricted the direct photocatalysis reaction on metal surfaces; however, the energy obtained as a result of recombination facilitated thermal reaction and resolved this drawback [167]. Since the foremost discovery of primary photocatalysis by Au NPs through LSPR [168], numerous reactions have been performed on Ag, Au, and Cu surfaces, showing that low intensity visible photon irradiation significantly enhances the rate of chemical reactions. A pioneering work showed that Au NPs have potential in degrading volatile organic compounds, HCHO to CO_2, under 600–700 nm red light irradiation [168]. The same group also reported the use of Ag NPs to remove phenol and drive oxidation of benzyl alcohol to benzaldehyde under UV light. This verifies the role of the LSPR effect and interband transition of Ag NPs in activating organic molecules for oxidation under UV–vis irradiation [169]. Au NPs are more suitable for immediate plasmonic photocatalysis compared to other plasmonic metals because they are more chemically resistant and stable to standard atmosphere [170]. Under LED excitation at 530 nm in the presence of air or oxygen, Au NPs could promote the oxidation reaction of 9- anthraldehyde to form anthraquinone as the dominant product [171]. As compared to semiconductors like TiO_2, the ability of Au NPs to conduct plasmonic-induced reductions at lower temperature and pressure enable the selection of unstable intermediates of a thermal reaction as the product (e.g., aromatic azo compounds). These findings show the potential of Au NPs in utilizing the solar spectrum, also in temperature-sensitive synthesis [172]. Most reported works on direct photocatalysis are limited only to plasmon-induced chemical transformations. Very few have moved away from this traditional route to demonstrate the feasibility of electrocatalytic oxidation adopting glucose accelerated by Au NPs upon LSPR excitation under a suitable voltage bias. The hot electrons injected from Au NPs can be driven into the external circuit to deliver appreciable current, while the holes facilitate the electrocatalytic oxidation of glucose owing to their equal energy levels. This constructive finding propelled the potential applications of electrochemical energy conversion, electroanalysis and electrochemical devices [173]. Overall, it is clear that the plasmonic metals are able to concentrate and channel the energy of low intensity visible light into adsorbed molecules to promote significant enhancement in the rate of chemical transformation. Furthermore, there are certain cases that have showed primary evidence for direct plasmon-driven photocatalysis capable of controlling catalytic selectivity through different reaction mechanisms. Gold NPs on CeO_2 were found to be efficient at reducing a wide range of epoxides, azo compounds, and ketones at ambient temperature under visible light. Their reduction potential highly depends on the incident wavelength [174]. The team revealed the selectivity tuning by plasmon-mediated photo-switching and demonstrated the same for propylene epoxidation on Cu NPs in which the reduction of the Cu_2O shell was brought on by the plasmon-excited Cu [175].

Conclusion

This review explicitly detailed insight into plasmonic photocatalysts as a potential candidate for enhanced utilisation of the solar spectrum. The topic of the review was detailed through fundamental explanations together with the various synthesis routes. The review also clarified the mechanism of LSPR for the various noble metal nanoparticles in addition to the Schottky phenomenon on the studied metal oxide photocatalysts. An in-depth analysis on the formation and identification of ROSs and their interaction with pollutants was clearly presented. The future prospects of these sustainable photocatalysts with real-time applications for energy storage and environmental remediation were thoroughly reviewed. The present review also revealed the potential of plasmonic photocatalysts as an alternative sustainable approach and new direction for effectively harnessing sunlight to fulfil global environmental issues and aid to the energy crisis.

Acknowledgements

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4. Conclusion

The synergetic N-TiO_2/AC composites have been successfully synthesized. The prepared photocatalysts had a better absorbance towards the visible region ensuring the utilization of the solar irradiation. The synergetic effect was also well observed in terms of adsorption and contributed for the better removal of RBB dye. Thus shows the significance of the developed synergized photocatalysts. On the whole the prepared N-TiO_2/AC exhibited its vibrant applicability towards wastewater treatment by incorporating both the sorption and photocatalytic effect.

Acknowledgement

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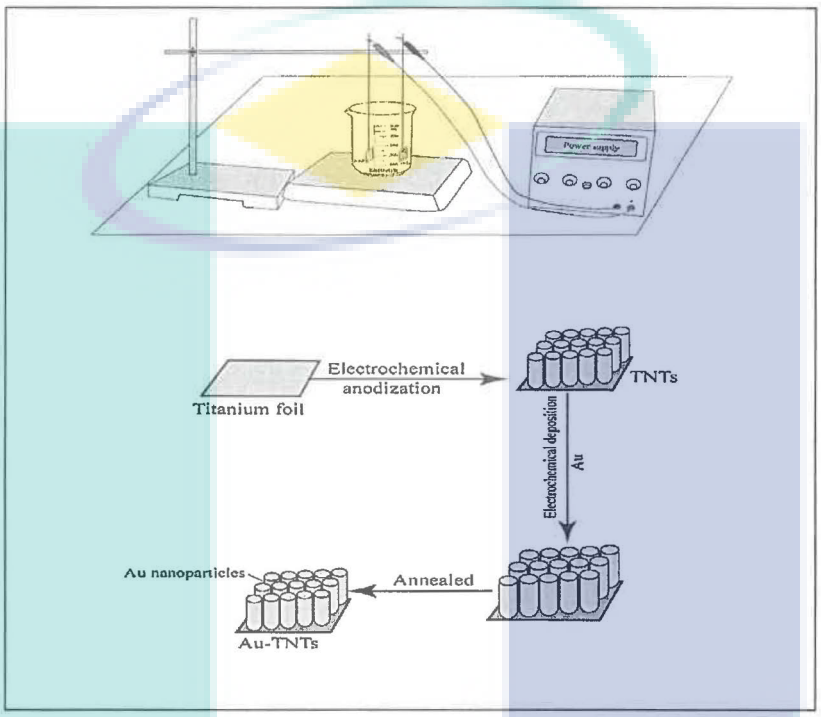
LAMPIRAN B

TEMPLATE
BUKU PROFIL PENYELIDIKAN SKIM GERAN PENYELIDIKAN GERAN UNIVERSITI JANGKA PENDEK / GERAN DALAM UMP (LAPORAN AKHIR)



DEVELOPMENT AND MODIFICATION OF TIO2 BASED-NANOPHOTOCATALYST FOR DIRECT CONVERSION OF CO2 TO HYDROCARBON FUEL

Name of Project Leader : Prof. Madya Dr. Azrina Abd Aziz
Name of co-researchers : Prof. Madya Dr. Muzamir Hasan,
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Field : Technology and Engineering

ABSTRACT (120 words)

Malaysia has huge coal reserves that can be fully tapped as an additional source of energy to lessen the burden of domestic industries currently saddled with increasingly high energy costs from gas and electricity. According to the Mineral and Geoscience Department, the country's coal resources are estimated at 1.72 billion tonnes, of which 274 million were measured, 347 million indicated and the balance 1.1 billion inferred. Even though coal is a national treasure, managing CO_2 emissions from its utilization is perhaps the largest technical challenge currently faced by the fossil energy industry. Although CO_2 is routinely captured from the conventional industrial processes includes ammonia production and limestone calcination, existing capture technologies are not economical for use in power plants. As such, transformational new technologies are needed to help and address the CO_2 challenges. Moreover most of the work on reducing the concentration of anthropogenic carbon dioxide in the atmosphere is focused on either reducing the emissions from fossil fuel combustion or capturing and sequestering the resulting carbon dioxide. There is, however, a third possible path: the conversion of CO_2 back to a hydrocarbon fuel.

1. INTRODUCTION

There is depiction of integrated solar fuels system, where sunlight is used to convert CO_2 and water vapor into hydrocarbon fuels. Such fuels can be stored or transported as needed and, when used, result in CO_2 formation that is then passed to the photocatalytic array where it is converted back to fuel. One of the earliest reports on photoelectrochemical reduction of carbon dioxide was published by Halmann in 1978[1] An electrochemical cell was used, composed of a single crystal p-type GaP cathode, carbon anode, and a buffered aqueous electrolyte through which carbon dioxide was bubbled. When the GaP crystal was illuminated (mercury lamp) and a voltage bias applied, current was detected, with the electrolyte solution showing the presence of formic acid, formaldehyde, and methanol. Many research groups have since investigated the use of different compound semiconductors to achieve higher visible light catalytic activities. Using p-GaAs and p-InP photoelectrodes in a CO_2-saturated solution of Na_2SO_4, Canfield and Frese achieved CO_2 re duction to methanol. Similarly, formation of metha nol together with formic acid and formaldehyde was reported by Blajeni et al., 1983 using single- crystal p-GaP and p-GaAs photoanodes.[2] Eggins and co-workers reported visible light photoreduction of CO_2 in the presence of colloidal CdS in an aqueous solution of tetramethylammonium chloride, yielding glyoxylic acid as well as for mic and acetic acids and CH_2O.[3] Fujiwara and co- workers studied the use of ZnS nanocrystals as visible light photocatalysts, finding that excess metal ions enhanced the photocatalytic response, a behavior attributed to the formation of sulfur vacancies that acted as catalytic sites for CO_2 reduction.[4] In 1979, Inoue and co-workers [5] examined the use of semiconductor powders for CO_2 reduction, including TiO_2, ZnO, CdS, SiC, and WO_3, suspended in CO_2 saturated water illuminated by a Xe lamp. Small amounts of formic acid, formaldehyde, methyl alcohol and methane were produced. Anpo and Chiba reported the use of highly dispersed titanium oxide on glass for the photocatalytic reduction of carbon dioxide [6].UV illumination of the catalyst in the presence of CO_2 and H_2O resulted in the photocatalytic formation of CH_4, CH_3OH, and CO as major products. From the direct detection of intermediate species, they proposed that methane formation resulted from the reaction between carbon radicals and atomic hydrogen, with the photoreaction efficiency strongly dependent upon the CO_2 to H_2O ratio and reaction temperature. The charge transfer excited state, Ti–O of the tetrahedral coordinated titanium oxide species, was found to play a critical role in determining the

photoreactivity. The use of Cu as a Co catalyst in combination with TiO2 resulted in methanol formation. In another report Anpo et al. examined photocatalytic reduction of CO_2 and water vapor at 328 K using titania- loaded zeolite, which demonstrated a high selectivity for gas phase methanol formation. Addition of Pt to the TiO_2 led to an increased methane yield compared to methanol formation [6] Using sunlight to convert CO_2 and water vapor into hydrocarbon fuels that are compatible with the current energy infrastructure. Ideally, such solar energy powered photocatalytic materials, used on a closed-loop basis can be used to recycle CO_2 from a climate altering waste product into a fuel. While encouraging progress has been achieved toward photocatalytic conversion of CO_2 using sunlight, further effort is required for increasing sunlight-to-fuel photo conversion efficiencies. In all the above studies the conversion rate of hydrocarbon was the major limitation. Therefore in the present study a novel TiO_2 photocatalyst will be prepared for the higher conversion of CO_2 to hydrocarbon by using the sunlight source. The proposed objective is most challenging in the catalysis field, since it aims to developing/preparing a novel doped photocatalyst with high visibility property for the better conversion of CO_2 to Hydrocarbon. Moreover the research is in high demand in the G7 countries, since it is more sustainable and provided an excellent solution to the global warming pollutant.

2. RESEARCH METHODOLOGY

Synthesis of Visible Light Photocatalyst (attached flowchart) Catalyst: TiO2 based catalyst with suitable dopant such as quantum dots/Pt/graphene/etc

Synthesis Technique: Reverse miscelle/Sol-gel/CVD

Characterization:

1) The prepared nano photocatalyst will be characterized to confirm the synthesis reaction, product obtained and the activity of obtained product.

2) The morphology, crystalline peak position, grain size, surface area, pore size distribution, spectral absorbance and finally functional group analysis has to performed.

3) After evaluating all the characters, if required further modification for enhancing the catalyst performance could be done in the synthesis procedure. Photocatalytic Conversion Study: CO2 to Hydrocarbon Fuel (attached experimental setup)

4) The finally synthesized materials would be evaluated for the photocatalytic conversion of CO2 to hydrocarbon under the solar light.

5) The conversation rate will be optimized: Laboratory Scale.

6) The converted hydrocarbons will be quantified with Gas Chromatography

3. LITERATURE REVIEW

The photocatalytic conversion of carbon dioxide (CO_2) into hydrocarbon fuels with the input from ultraviolet (UV), visible light/solar energy is a promising and eco-friendly approach to prevent the increasing levels of greenhouse gases and depletion of fossil resources. To best acknowledge, photocatalysts viz., TiO_2 emerged as an ideal candidate over CdS, ZrO2, ZnO and MgO due to its versatile characteristics including non-toxicity, high photo-stability, chemical biologically inert and higher photoactivity [1].However, the robust stability of CO_2 poses an indeed challenge to surpass its energy barrier and thus lowering the efficiency of CO_2 photoreduction with water [2,3]. Numerous efforts have been devoted to improve CO_2 reduction efficiencies from the point of light harvesting and charge carriers separation enhancement [4].Additionally, adsorption capability of CO_2 on the surface of photocatalyst and the efficient transport of photoinduced electron toward CO_2 are also the key factors for enhanced photoconversion efficiency. In order to oblige to the above key factors, one dimensional TiO_2 nanotube arrays (TNTs) possess great potential over the nanoparticle form owing to its higher surface-to-volume ratios, attractive surface nature, superior charge mobility and durable chemical stability [5].

Recently, researchers focused on the development of modified TiO_2 nanoparticles or nanotube arrays for such application. All these studies utilized wide range of metals, non-metals or combinations of both as impurities [6-9]. Among them, noble metals unveil more versatility than the rest and excel as an electron trapper. Off all noble metals, Pt/Ag/Au nanoparticles (NPs) are well supported for its functionality as an electron trapper which further anchored the separation of photogenerated electron–hole pairs [10-11]. On the other hand, it also possesses great visible light absorption properties which were correlated with the oxygen vacancies, Ti3+ ions and Pt/Ag/Au impurities (e.g. Pt0, Pt2+, and Pt4+) created at the titania surface [12-13]. Li et al. found that the loading of Pt on TiO_2 porous films expanded the UV light absorption ability and improved the transformation efficiency of CO_2 to methane (CH_4) with a better yield [10]. The Pt-nanoparticle/TiO_2 nanotube composite was shown to greatly promote the photocatalytic conversion of CO_2 to CH_4 with production rate of about 36 ± 6 μL g−1h. This was due to a uniform homogeneous distribution of Pt NPs over the TiO_2 nanotube array surface thus providing large number of active reduction sites [10]. Similarly, a maximum CH_4 yield of 1361 μmol g cat−1h−1 was achieved by Wang et al. through TiO_2 nanotubes coated with Ag NPs [6]. When Pt NPs were used in combination with Ag@SiO_2/TiO_2, 80% selectivity of CH_4 was attained over TiO_2 that resulted in 20% [14]. Pt NPs were applied as an electron transporter to transfer the electrons which were excited by the LSPR effect in Ag@SiO_2. In the photocatalytic conversion of CO_2, Pt NPs were mostly utilized but their visible light properties still remain largely unexplored.

Among the non-metals category, graphene a two-dimensional sp2-hybridized carbon nanosheet has attracted the researchers either as individual or hybridized with metal/metal oxides to further catalyze the electron transport. This graphene contributes for high specific surface area, great electron mobility and tunable band gap [15]. Tan et al. demonstrated that the less defective graphene–TiO_2 nanocomposite resulted in larger photocatalytic enhancement for the photoreduction of CO_2 to methane (CH4) [16]. Aleksandrzak et al. reported that graphene–TiO_2 nanocomposite utilizing UV light achieved a maximum CH_4 product yield of 0.135 μmol g cat−1h−1, which is 2.1 and 5.6 fold higher than that of graphite oxide and pure anatase [17]. These studies unlocked the enhancing effects of graphene on the photocatalytic properties of TiO_2 was attributed to

large surface area, adsorption capacity and strong electron transfer ability of graphene in hybrid materials.

So far, there is no current reported study investigated on the reduced graphene-noble metal incorporated with TNTs for photocatalytic conversion of CO_2 under visible light. Therefore, the present study has following benefits over the reported: (1) a facile and low cost method to reduce GO into graphene (RGO) nanosheets and assemble them onto Pt/Ag/Au–TNTs, (2)the photocatalytic performance was evaluated under visible light irradiation instead of UV light to explore the LSPR effect of Pt/Ag/Au NPs.

4. FINDINGS

Development of new photocatalyst with potential in energy conversion. This project is in line with government National Priority Area (NPA) on energy by investigating the harnessing alternative resources on improving the efficient use of energy especially in the areas of renewable energy to reduce dependency on fossil fuel.

5. CONCLUSION

Contribute to the economy of national environmental sector. This sorts of green sustainable method can economize energy and contribute for the nation greenhouse gas reduction.

ACHIEVEMENT

i) Name of articles/ manuscripts/ books published
   a) Mechanistic Insights Into Plasmonic Photocatalysts In Utilizing Visible Light
   b) Preparation of Activated Carbon/N-Doped Titania Composite For Synergistic Adsorption Photocatalytic Oxidation of Batik Dye

ii) Title of Paper presentations (international/ local)
   a) Preparation of Activated Carbon/ N-Doped Titania Composite For Synergistic Adsorption-Photocatalytic Oxidation of Batik Dye

iii) Human Capital Development
   1 Master Non- Malaysian student graduated.

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