PHOTOCATALYTIC WATER SPLITTING OVER TITANIUM ALIMINIUM CARBIDE ASSISTED RUTHENIUM WITH GARPHITIC CARBON NITRIDE FOR HYDROGEN PRODUCTION

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ABSTRACT

Photocatalytic water splitting for hydrogen production is considered to solve the issue of greenhouse gases and other environmental concerns as hydrogen is considered as an alternative source of energy that can replace fossil fuel. The objective of this study is to develop ternary photocatalyst functional under visible light for water splitting to generate hydrogen. Titanium aluminium carbide (Ti_3AlC_2) dispersed ruthenium (Ru) doped graphitic carbon nitride (g-C_3N_4) composite (Ti_3AlC_2/Ru/g-C_3N_4) was developed using hydrothermal assisted impregnation method followed by characterization including XRD, SEM, TEM, Raman, UV-visible and PL spectroscopy techniques. The function of g-C_3N_4 is to enhance visible light harvesting, while Ti_3AlC_2 developed Z-scheme hetero-junction for fast charges separation as a result more electrons were produced for H^+ to H_2 reaction. The photocatalytic activity was tested using slurry photo-reactor systems for continuous H_2 production. Ti_3AlC_2/Ru/g-C_3N_4 composite was observed to produce 1665 µmolg^{-1}h^{-1} of H_2 with each gave 1.3 and 1.93 times higher than produced from Ru/g-C_3N_4 and Ti_3AlC_2/g-C_3N_4 samples, respectively. This enhanced hydrogen production was obviously due to superior photogenerated charges separation with higher visible light absorption and developing Z-scheme heterojunction. The operating parameters such as varying catalyst loading, various sacrificial reagents and irradiation time were investigated. Besides, the stability of catalyst over 3 continuous cycles was also studied. The highest yield rate of hydrogen production was for 0.25 g catalyst loading. H_2 production by using different sacrificial reagents was in order: water < glycerol < ethanol < ethylene glycol < methanol. In conclusion, excellent performance of composite catalyst using a slurry reactor for H_2 production would offer a new opportunity of developing structured photocatalysts for renewable fuels production under visible light.

ABSTRAK

Pembelahan air fotopemangkinan untuk penghasilan hidrogen dianggap penyelesai masalah gas rumah hijau dan kebimbangan lain alam sekitar kerana hidrogen dianggap sebagai sumber alternatif tenaga yang dapat menggantikan bahan api fosil. Objektif kajian ini adalah untuk membangunkan fungsi fotopemangkin ternari di bawah cahaya nampak untuk pembelahan air bagi menjana hidrogen. Komposit (Ti_3AlC_2/Ru/g-C_3N_4) titanium aluminium karbida (Ti_3AlC_2) terserak rutenium (Ru) didopkan karbon grafit nitrida (g-C_3N_4) dibina menggunakan kaedah pengisitepuan berbantu hidroterma diikuti dengan pencirian termasuk XRD, SEM, TEM, Raman, UV-nampak dan teknik spektroskopi PL. Fungsi g-C_3N_4 adalah untuk meningkatkan cahaya nampak manakala Ti_3AlC_2 membina hetero-simpang skema-Z untuk pemisahan caj dengan cepat dan menyebabkan lebih banyak elektron dihasilkan untuk tindak balas H^+ ke H_2. Aktiviti fotopemangkinan diuji menggunakan sistem foto-reaktor untuk penghasilan H_2 berterusan. Komposit Ti_3AlC_2 / Ru / g-C_3N_4 didapati menghasilkan 1665 $\mu molg^{-1}h^{-1}$ H_2 dengan masing-masing memberi 1.3 dan 1.93 kali lebih tinggi berbanding dengan yang dihasilkan oleh sampel Ru/g-C_3N_4 dan Ti_3AlC_2/g-C_3N_4. Penghasilan hidrogen tertingkat ini jelas disebabkan oleh pemisahan caj fotogenerasi yang unggul dengan penyerapan cahaya nampak yang lebih tinggi dan membangunkan hetero-simpang skema-Z. Parameter operasi seperti muatan pemangkin yang berbeza-beza, pelbagai reagen korban dan masa penyinaran dikaji. Selain itu, kestabilan pemangkin terhadap 3 kitaran berterusan juga dikaji. Kadar hasil tertinggi penghasilan hidrogen adalah bagi 0.25 g muatan pemangkin. Penghasilan H_2 dengan menggunakan reagen korban berbeza adalah dalam turutan: air <gliserol <etanol <etilena glikol <metanol. Kesimpulannya, prestasi cemerlang pemangkin komposit menggunakan reaktor buburan untuk penghasilan H_2 akan menawarkan peluang baharu membangunkan fotopemangkinan berstruktur untuk penghasilanan bahan api yang boleh diperbaharu di bawah cahaya nampak.

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LIST OF ABBREVIATIONS

ALD	-	Atomic Layer Deposition
CB	-	Conductance Band
FESEM	-	Field Emission Scanning Electron Microscopy
GHG	-	Greenhouse gas
PL	-	Photoluminescence
SEM	-	Scanning Electron Microscopy
TEM	-	Transmission Electron Microscopy
UV	-	Ultra-Violet
VB	-	Valance Band
XRD	-	X-ray Diffraction
$g\text{-}C_3N_4$	-	Graphitic carbon nitride
Ti_3AlC_2	-	Titanium aluminium carbide

LIST OF SYMBOLS

W	-	Watt
g	-	Gram
mol	-	Mole
λ	-	X-ray Wavelength
e^-	-	Electron
h^+	-	Hole
Eg	-	Energy band gap
E_c	-	CB Minimum Energy Level Position
E_v	-	VB Maximum Energy Level Position

CHAPTER 1

INTRODUCTION

1.1 Background

Recently, the world is facing challenges of excessive greenhouse gases (GHG) emission that increases the average temperature of the earth and is main cause of global warming. Also, fossil fuels are considered main cause of environmental issues because of their excessive use leading to emission of CO_2 [1]. Transportation is also a part of energy consumption that causes emissions of greenhouse gases in the atmosphere [2]. Currently, 65% of worldwide energy demand is fulfilled by utilization of fossil fuels due to their high energy content. However, over the time, fossil fuels will be depleting as they are considered as non-renewable source of energy [3]. Therefore, alternative renewable energy sources have been developed to replace fossil fuels. Hydrogen energy is considered as renewable energy and is expected to have potential for fulfilling energy demands in coming years.

There are various technologies to generate H_2 such as thermal, electrical, photonic and biochemical energy. These techniques have disparate properties, and some of them will be the best choice to generate H_2. Thermal technique produces a huge amount of H_2, but it is using non-renewable energy sources like fossil fuel. Although, electrical method uses a renewable source to generates H_2, this process is expensive. Biochemical energy converts biomass support by microorganism into H_2, which is called biological process [4]. The best method to generate H_2 is photonic as it is an abundant energy resource, which uses light irradiation that comes from the sun, so we can say that this the best technique.

Photocatalytic system depends on photonic energy that is released from light irradiation and converted into chemical energy. This process is better than other technologies because it is considered to be more economical than the others. Solar irradiation is abundant in nature and it is easy to get compared with heat energy. Water splitting occurs when photocatalysis process produces photonic energy and give catalyst high stability. Furthermore, this process is economic because it relies on solar energy and water that are abundant resources on our planet. Also, this energy is sustainable and environmentally safe [5].

Nowadays, photocatalysis involved in hydrogen production has attracted the attention of researchers. The components of photo-catalysis are reactant, photocatalyst, photo-reactor and light irradiation. Among the semiconductors, titanium dioxide has been widely used in photocatalytic water splitting due to high chemical and thermal stability. However, TiO_2 has limitations such as UV-active only and faster charges recombination, resulting in lower hydrogen production. Therefore, efficient and stable catalysts functional under solar energy are highly demanding to develop sustainable system for solar hydrogen production.

Recently, MAX phase compounds are under exploration in various applications. The formula of this compound is $M_{n+1}AX_n$ with n=1 to 3, where X is either nitrogen or carbon, A is mostly groups 13, 14 element and M is an early transition metal. Ti_3AlC_2 has metallic-covalent-ionic bonds that have many features of both metal and ceramics. On the other side, polymeric graphitic nitride (g-C_3N_4) is considered as one of the most popular photocatalysts that has been investigated by researchers. g-C_3N_4 can respond perfectly to the visible light because it has band gap 2.7 eV. This photocatalyst is easy to synthesise because the materials used to prepare it, such as melamine and urea, are low cost. It has many properties such as high thermal/chemical stability but fast recombination rate of charges and low surface area [6, 7]. The bond between carbon and nitrogen in g-C_3N_4 is very strong, which cause excellent photo-corrosion resistance [8]. With a view to increase the efficiency of H_2 production, it can be coupled with other metals. Among all the metals, Ruthenium (Ru) is one of the noble metals and is considered as good metal dopants. Ru significantly promotes the separation of photogenerated electron-hole pairs and extends the photo absorption toward the visible light regime arising from the formation of an intermediate energy level [9].

In this study, design and development of novel nanocomposite photocatalyst to investigate photocatalytic hydrogen production has been investigated. The composite Ti_3AlC_2/Ru/g-C_3N_4 was found very efficient to give high yield of hydrogen under visible due to faster separation and utilization of charge carrier under visible light irradiations.

1.2 Problem Statement

Hydrogen production by water splitting has become popular in recent years, but it presents some problems and troubles such as low yield of hydrogen production under visible light. Followings are the problems and research hypothesis of this work:

(i) Polymetric graphitic nitride (g-C_3N_4) is considered as one of the most popular photocatalysts that have been investigated by many researchers. This catalyst can respond perfectly to the visible light because it has band gap 2.7 eV. It has many properties such as high thermal and chemical stability. However, it has limitations such as fast charges recombination rate and low surface area. The photoactivity of g-C_3N_4 can be improved by coupling with other materials. Among the 2D materials, titanium aluminium carbide (Ti_3AlC_2) is a layered material of MAX phase having energy applications with advantageous layered structure providing increased surface area and active sites for reduction reaction leading to increase H_2 production. Thus, coupling g-C_3N_4 with Ti_3AlC_2 would develop 2D/2D heterojunction of Z-scheme system to maximize hydrogen production.

(ii) With a view to increase the efficiency of H_2 production, the composite of g-C_3N_4 can be coupled with other metals. Ruthenium is one of the noble metals and considered as good metal dopants. Ru significantly promotes the separation of photogenerated electron-hole pairs and extends the photo absorption toward the visible light regime arising from the formation of an intermediate energy level. Ru also can improve the electron conductivity which would be beneficial for maximizing hydrogen production.

(iii) The fabrication of the novel ternary Ti_3AlC_2/Ru/g-C_3N_4 nanocomposite is expected to develop Z-scheme photocatalytic system which would increase the yield rate of hydrogen production. Optimizing the parameters such as loading of the catalyst, sacrificial reagent and reaction time would be helpful to enhance hydrogen production rate.

1.3 Objectives of Study

In this work catalysts synthesis and characterization for photocatalytic hydrogen production has been investigated. Thus, specific objectives for this study are:

(i) To synthesis and characterize ternary Ti_3AlC_2/Ru/g-C_3N_4 nanocomposites functional under visible light,

(ii) To investigate the performance of newly developed photocatalyst in photocatalytic water splitting and investigation of different parameters for the photoactivity of composite to maximize H_2 production,

(iii) To suggest reaction mechanism of recently developed composite for photocatalytic water splitting under visible light.

1.4 Scope of Study

In this work, initially, catalysts were synthesized and then characterized. In the next stage, performance analysis was conducted under visible light irradiations. The parameters were conducted to maximize composite catalyst performance. Thus, scope is this work is as follows:

(i) Photocatalyst g-C_3N_4 was prepared using hydrothermal and simple mixing methods. The composite Ti_3AlC_2/Ru/g-C_3N_4 synthesised by mixing the sample g-C_3N_4 with Ti_3AlC_2 then Ru. The samples were characterized using various techniques such as XRD, Raman, EDX, TEM, PL spectra and UV-Visible Spectrophotometer.

(ii) The performance of Ti_3AlC_2, g-C_3N_4, Ru/g-C_3N_4, Ti_3AlC_2/g-C_3N_4 and Ti_3AlC_2/Ru/g-C_3N_4 composite were investigated for H_2 production under visible light irradiation. Operating different parameters were determined to find the best way to increase the yield such as catalyst weight, sacrificial reagent and time of the irradiation.

(iii) After proper analysis and study of results obtained, reaction mechanism of the composite which electrons transfer between semiconductors from conduction band (CB) of higher negative to CB of lower negative while Z-scheme system transfer electron from CB of lower negative to valence band (VB) of lower positive semiconductor through solid mediator proposed.

1.5 Significance of Study

This study is important for many reasons. First, the research on Ti_3AlC_2/Ru/g-C_3N_4 assures that this catalyst can be used under low light and guidance on mechanism of the composite during water splitting. Various parameters on water splitting will be applied to represent the effect which will give much comprehension on this study. This research illuminates that photocatalyst have many features such stability, high charge separation and ecological.

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