Enhance photocatalytic of hydrogen production from water-glycerol solution over RuO$_2$-loaded

H Husin$^{1,2*}$, K Pontas$^{1,2}$, M Zaki$^1$, D Darmadi$^{1,2}$ and A Masna$^1$

$^1$Graduate Program in Chemical Engineering, Syiah Kuala University, Darussalam, 23111, Banda Aceh, Indonesia
$^2$Department of Chemical Engineering, Syiah Kuala University, Darussalam, 23111, Banda Aceh, Indonesia

*husni_husin@che.unsyiah.ac.id

Abstract. Study of hydrogen production from aqueous glycerol solution on RuO$_2$-loaded LaNaTaO$_3$ has been studied. This research aim is to investigate the influence of co-catalyst RuO$_2$ and glycerol as a sacrificial reagent on the photocatalytic process of hydrogen production. La-doped NaTaO$_3$ was prepared via sol-gel route. The RuO$_2$ was loaded onto the LaNaTaO$_3$ surface by impregnation method. The sample was characterized by Scanning Electron microscopy (SEM) and X-ray Diffractometer (XRD). From XRD spectrum shows that the La-NaTaO$_3$ photocatalyst has high crystallinity. The SEM analysis indicates that the size of La-NaTaO$_3$ photocatalyst is ranging from 100 to 250 nm without agglomeration and RuO$_2$ as a co-catalyst is well loaded into the La-NaTaO$_3$ surface. The rate of hydrogen production increased significantly with a glycerol concentration. Loading RuO$_2$ on La-NaTaO$_3$ photocatalyst is proved to increase the rate of hydrogen production of 3.2 times with the addition of glycerol as a sacrificial reagent. The highest hydrogen production activity was obtained for 0.3 wt.% ruthenium loading. The role of co-catalyst RuO$_2$ and glycerol as a sacrificial reagent has enhanced the performance of La-NaTaO$_3$ photocatalyst since both play an active role in the separation efficiency of electrons and holes and the reaction of hydrogen formation.

1. Introduction
The technologies of hydrogen production have widely used today are steam reforming and water electrolysis. The steam reforming process requires enormous energy and still use fossil-based materials as its fuel thus the process still produces environmental pollutant gases such as carbon dioxide. While the water electrolysis method, even using renewable sources but requires large electrical energy. So that the various researches focused on the utilization of renewable sources such as water and biomass derivatives to produce hydrogen with cheaper alternative technology, energy efficient and environment-friendly [1-3].

An alternative technology for producing hydrogen is photocatalytic water splitting using semiconductors as its catalyst. A semiconductor is called a photocatalyst because it has the ability to absorb photon energy. Photocatalytic has been studied extensively as a clean technology since it uses solar energy to produce hydrogen from water and does not produce environmental pollutants [4,5]. The most widely used photocatalyst are metal oxide-based semiconductors, one of which is sodium tantalum...
oxide (NaTaO$_3$) which is one of the most efficient photocatalyst in producing hydrogen from water [6-11].

The photocatalytic reaction of the water decomposition on the surface of photocatalyst NaTaO$_3$ has an advantage because of its high activeness to light and aqueous solution. However, there are some problems found in such photocatalytic reactions that are low efficiency because NaTaO$_3$ have large band gaps (4.10 eV), recombination between photo-generated electrons - holes and back reaction between H$_2$ and O$_2$ on the surface of NaTaO$_3$ photocatalyst. The addition of dopants into NaTaO$_3$ crystalline structure can narrow down the band gap and improve its photocatalytic ability [12]. The ability of NaTaO$_3$ photocatalyst can be enhanced by the addition of Lanthanum (La) dopant. La dopant is useful for the preparation of NaTaO$_3$ in fine particle sizes with high crystallinity even it prepared at high calcination temperatures. The surface area of photocatalyst must be increased with the reduced particle size. Doping La can reduce the particle size of NaTaO$_3$ from 2-3 μm to 0.1 - 0.7 μm [13,14]. The surface area affects the number of active sites, while the particle size affects the distances travelled by the photo-generated electrons and holes in migrating to the photocatalyst particles to reach the active site.

Recombination between electrons - holes and reverse reaction between H$_2$ and O$_2$ can be prevented by using donor electrons or sacrificial reagents that can react with the formed O$_2$ or photo-induced holes. The electron donor which potentially used is glycerol because it has Gibbs-free energy of hydrogen production smaller than water splitting. While loading of metal co-catalysts such as ruthenium oxide (RuO$_2$) on the photocatalyst surface is required to capture the generated electrons in order to increase photocatalytic activity [15-18].

This study focuses on evaluating the influence of loading RuO$_2$ co-catalyst on La-doped NaTaO$_3$ photocatalyst and glycerol concentration as an electron donor or sacrificial reagent to the rate of hydrogen production on photocatalytic water splitting.

2. Experimental

2.1. Material

The materials and reagents used in this study are Tantalum Chloride (TaCl$_5$, Acros Organics: 99.9%), Sodium Hydroxide (NaOH, Acros Organics: 99.9%), La (NO$_3$)$_3$.2H$_2$O (99.9%), Citric Acid (C$_6$H$_8$O$_7$, Acros Organics: 99.5%), Ethanol (C$_2$H$_5$OH, 99%), Ru$_3$ (CO)$_12$ (Aldrich, 99%) (as ruthenium precursor), glycerol solution (C$_3$H$_5$O$_3$), and ammonia solution (NH$_4$OH, Fisher Scientific: 35%), and distilled water.

2.2. Preparation of La-NaTaO$_3$

The preparation of La-doped NaTaO$_3$ photocatalyst followed the procedure in the previous study [19], through a sol-gel procedure using ethanol as solvent. Synthesis is carried out as follows: 1.5 grams of tantalum chloride (TaCl$_5$) was dissolved in 150 ml ethanol and NaOH was dissolved in 50 ml distilled water. Then these two solutions are mixed using magnetic stirrer (solution A). 0.0362 grams of La(NO$_3$)$_3$.2H$_2$O was dissolved into 15 ml distilled water then added to solution A. The mixture was stirred with a magnetic stirrer (solution B). 4 grams citric acid (C$_6$H$_8$O$_7$) as chelating agent is dissolved in 50 ml distilled water and then dripped into solution B to produce the sol solution while stirring constantly at room temperature. The pH of the solution was adjusted to 4 using NH$_4$OH solution. The mixture was then heated and the temperature is kept constant at 90°C until a white gel is formed. The gel was dried in an oven at 110°C, then pre-heated at 450°C for 4 hours and finally heated at 900°C calcination temperature for 10 hours with flowing air into the reactor to increase crystallinity.

2.3. Loading co-catalyst ruthenium

Loading co-catalyst on the surface of La-doped NaTaO$_3$ catalyst was carried out by the impregnation method following the NO$_x$ impregnation procedure in the previous study [20]. Co-catalyst was prepared by dissolving precursor of Ru$_3$(CO)$_12$ into distilled water and then deposited on the La-doped NaTaO$_3$ photocatalyst surface by an impregnation method to promote H$_2$. The weight of platinum with variations
of 0.1\%, 0.2\%, 0.3\%, 0.4\%, and 0.5\% of Ru\(_3\)(CO)\(_{12}\)O were dissolved in distilled water then mixed with 1 gram of La-doped NaTaO\(_3\) photocatalyst. The mixture was stirred for approximately 6 hours at room temperature. Ruthenium-loaded La-doped NaTaO\(_3\) was heated in an oven at 110°C, then calcined with air at 300°C for 2 h. The photocatalyst characterization was analysed by X-ray Diffraction (XRD) method, with a Shimadzu 7500 X-ray advanced diffractometer with Cu-K\(\alpha\) radiation (\(\lambda = 1.5406 \text{ Å}\)). The accelerating voltage and the applied currents were 40 kV and 40 mA, respectively. The shape and morphology of the sample were identified by Scanning Electron Microscopy with a JEOL 5600 SEM. HRTEM images were recorded by a JEOL Model JEM 2010 EX instrument at an accelerating voltage of 200 kV.

2.4. Photocatalytic reaction
The photocatalytic reaction was carried out in a pyrex glass reactor under UV radiation for hydrogen generation. Photocatalyst powders with different concentrations of 0.1; 0.5; 1.0; 1.5; 2.0 grams were dispersed into 350 ml aqueous solution of glycerol-water using a magnetic stirrer. Variations of glycerol concentration in water were 0%, 5%, 10%, 15%, and 20%. The irradiation source uses a 400-watt mercury lamp (\(\lambda \geq 250 \text{ nm}\)). Before the light illuminated, the air inside the reactor was removed with a flow of Argon gas. The reaction takes place at a temperature of 30°C for 3-5 hours. The amount of hydrogen production which is the test parameter in this study is measured using gas chromatography (Porapax N column and molecular sieve 5A, PDHID detector with helium gas).

3. Results and discussion

3.1. Characterization of RuO\(_2\)/La-NaTaO\(_3\) photocatalyst
Pt/La-NaTaO\(_3\) photocatalyst morphology analysis was performed using SEM (Scanning Electron Microscopy). Figure 1 shows the results of SEM analysis of La-NaTaO\(_3\) photocatalyst. It’s clearly shown that the form of La-NaTaO\(_3\) photocatalyst with particle sizes ranging from 100 - 250 nm.

The regular particle shape and small particle size are caused by the addition of lanthanum doping into the NaTaO\(_3\) lattice. This reinforces the facts as reported that the addition of lanthanum in NaTaO\(_3\) lattice can control the stability of the material and inhibit the agglomeration of NaTaO\(_3\) even though the preparation is carried out at high temperatures, besides lanthanum can also inhibit the formation of NaTaO\(_3\) particles in large size [21].

Figure 2 depicted a representative high resolution of transmission electron microscopy (HR-TEM) of RuO\(_2\)/LaNaTaO\(_3\) photocatalyst. It is clearly seen that RuO\(_2\) oxide particles in the range of 4 - 5 nm...
were well dispersed on the surface of La-NaTaO$_3$ with no aggregation. This is due to the amount of RuO$_2$ deposited on the surface of the photocatalyst is very small. A clean photocatalyst particle surface indicates RuO$_2$/La-NaTaO$_3$ photocatalyst particles having a high degree of crystallinity.

3.2. Crystal structure

Figure 3 shown XRD patterns of NaTaO$_3$ standard and La-NaTaO$_3$ sample. From Figure 3, it can be seen, both samples have the same profile. It is confirmed by 3 main characteristic peaks in the sample matching the 3 peaks of the NaTaO$_3$ standard powder data file. Those characteristic peaks are identified at 2θ: 22.7°, 33.6°, and 52.5° with the intensity of 33977.59 cps, 29636.75 cps, and 9414.01 cps, respectively. The crystallinity of the samples is greatly improved, as indicated by stronger and narrower XRD peaks in Figure 3.

Figure 3. XRD patterns of RuO$_2$/LaNaTaO$_3$.

3.3. Influence of glycerol concentration on hydrogen production rate

Figure 4 shows the rate of hydrogen production in pure water (without glycerol) of 0.58 (mmol/g$^{-1}$h$^{-1}$). The rate of production increased significantly in photocatalytic of the water-glycerol solution with glycerol concentration of 10 v/v% at 7.69 (mmol/g$^{-1}$h$^{-1}$)$^{-1}$. The rate of hydrogen production remained to increase in the tests with a variation of glycerol concentrations of 15 v/v% and 20 v/v%, reach of 10.77 (mmol/g$^{-1}$h$^{-1}$), and 12.6 (mmol/g.h$^{-1}$). These results indicate that the presence of glycerol in water greatly contributes to the process of photocatalytic by triggering the reaction of hydrogen formation to become more efficient.

The use of glycerol in the photocatalytic reaction process of hydrogen production is very promising, given the chemical structure of glycerol (C$_3$H$_8$O$_3$) has a much larger number of hydrogen atoms, so that the resulting hydrogen gas will be more, as shown in Figure 4. In the photocatalytic reactions process, glycerol acts as a sacrificial reagent or electron donor. The reaction in a dilute solution of glycerol takes place with the formation of intermediates such as glyceraldehyde, glycolaldehyde, acetic acid, glycine acid, and formaldehyde. Ultimately the full conversion of glycerol to hydrogen and carbon dioxide by the following reactions:

$$C_3H_8O_3 + 3H_2O \rightarrow 7H_2 + 3CO_2$$  \hspace{1cm} (1)

Theoretically (stoichiometric), the yield of H$_2$ produced is seven moles of hydrogen for every mole of glycerol reactant [15]. Glycerol as a sacrificial reagent or electron donor will react with holes in the valence band irreversibly to prevent the occurrence of recombination reactions.
Figure 5. Effect of various RuO$_2$ loading on hydrogen production; Reaction condition: Glycerol + water mixture of 350 ml, 10% of Glycerol, 0.3 g catalyst in the solution, UV light source.

Figure 6. Hydrogen production activity: Reaction condition: reaction glycerol + water mixture of 350 ml, 10% of glycerol, 0.3 g in the solution, UV light source.

Figure 5 shows the hydrogen production over various RuO$_2$ loaded La-NaTaO$_3$ photocatalysts at various amounts of RuO$_2$ loading levels containing 10% of glycerol. Ruthenium as a co-catalyst was loaded on the photocatalyst powder to promote H$_2$ production. The rate of hydrogen production has been found to be much higher, compared to that obtained from photocatalytic of pure water, as depicted in Figure 6. The rate of hydrogen production has been found to be much higher, compared to that obtained from photocatalytic of pure water. In the absence of glucose and RuO$_2$, the photocatalytic hydrogen generation is very low because of the recombination of photoinduced electrons and holes on a semiconductor surface [22].

4. Conclusions

RuO$_2$/LaNaTaO$_3$ crystal photocatalyst has been synthesized through the impregnation and sol-gel method. The SEM analysis indicates that the size of La-NaTaO$_3$ photocatalyst is ranging from 100 to 250 nm without agglomeration and RuO$_2$ as a co-catalyst is well loaded into the La-NaTaO$_3$ surface. Ruthenium as the nanosized co-catalyst trapping electron thus facilitates the separation of electrons and holes generated by the photocatalyst. Loading RuO$_2$ on La-NaTaO$_3$ photocatalyst is proved to increase the rate of hydrogen production of 3.2 times with the addition of glycerol as a sacrificial reagent. Glycerol can promote markedly photocatalytic hydrogen evolution RuO$_2$/La-NaTaO$_3$. Glycerol acting as an electron donor to scavenge photoinduced holes quickly so that the recombination of photoinduced electrons and holes at the RuO$_2$/La-NaTaO$_3$ surface and the back reaction of H$_2$ and O$_2$ are inhibited.

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