

Hydrogen production from water-glucose solution over NiO/La-NaTaO₃ photocatalyst

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Abstract. This paper reports the evaluation of La-NaTaO₃ photocatalyst performance in producing hydrogen from water-glucose solution. The main goal of the studies is to investigate the influence of glucose as a sacrificial reagent on the photocatalytic efficiency in water splitting reactions under ultraviolet (UV) irradiation. Photocatalyst has been fabricated via sol-gel method and being confirmed using x-ray diffraction (XRD) and scanning electron microscopy (SEM). Nickel loaded La-NaTaO₃ photocatalyst are prepared by impregnation method. It was observed that the prepared photocatalysts displayed particle sizes in the 30-250 nm range with orthorhombic structure. Their photocatalytic activity for hydrogen production via water splitting was conducted in a Pyrex glass reactor under UV light irradiation. The aqueous solution contained glucose employed as a renewable organic scavenger. A significant improvement in hydrogen production was observed in glucose-water mixtures and NiO loaded photocatalyst. The prepared La-NaTaO₃ showed that the highest activity for hydrogen generation of 35.1 mmol h⁻¹.g⁻¹ was obtained at 0.10 mol.L⁻¹ glucose and 0.3 wt.% NiO. This suggests the important role played by the glucose as electron donor and loading nickel on La-NaTaO₃ as a cocatalyst increasing electron storage and suppressing electron-hole recombination.

1. Introduction

Human civilization builds by an energy system which complexly integrated in which facilitated by an advancing technology to conduct an easier activity. It is important for us to have a breakthrough in an intensively researches to find, optimize, and use renewable resources. Now a days, an alternative energy resources is a big vision in most countries, especially in developing countries is hydrogen production from water [1]. Currently, over 50% of the world's hydrogen supply is from catalytic steam reforming (SR) of hydrocarbons [2-4]. Great efforts have been made in developing economical, environmentally friendly, and competitive processes for hydrogen production from renewable sources [5, 6].

Hydrogen has been considered as the chemical fuel of the future to replace fossil fuels as an energy resource in many fields. Through an intensive research, photocatalytic technology has been a

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prepared technology for producing hydrogen on a commercial scale which can be used as an alternative for energy source replacing fossil fuel. Photocatalytic process in hydrogen production using semiconductor photocatalyst has been intensely studied and that photocatalytic water splitting using oxide semiconductor as one of the promising schemes in producing hydrogen from water [7]. Semiconductor photocatalyst consists of an oxide or a sulfide. From various photocatalyst materials, NaTaO₃ oxide has been reported having excellence activity in producing hydrogen using UV lights. The addition of doping or strange substance into NaTaO₃ crystal structure can narrow band gap, increase crystallinity and smaller particle sizes, thus increasing the production level of hydrogen. Furthermore, the structure of the crystal photocatalyst also affecting photocatalysts band gap [8-11]. However, the efficiency of photocatalytic hydrogen evolution is in general very low due to the recombination of the photoinduced electron and hole, and the back reaction of H₂ and O₂. For the photocatalyst, to perform efficiently, the electron-hole recombination must be avoided.

To inhibit the above disadvantageous processes, an electron donor can be added into the reaction system as a hole scavenger to achieve high efficiency for hydrogen evolution. Many organic pollutants in wastewater are good electron donors. Methanol and glucose are known as a potential donor in decreasing the level of recombination for having Gibbs energy lower than water splitting ($\Delta G^\circ = 228.64 \text{ kJ.mol}^{-1}$). The success for glucose as a sacrificial reagent for rapidly increasing the rate for hole photo induction has been reported [12]. NiO_x has been found a more effective cocatalyst and it is necessary to provide an active site in photocatalytic of hydrogen production [13].

The aim of the present work is to study the influence of glucose as sacrificial reagents on photocatalytic efficiency in water splitting reactions under ultraviolet (UV) irradiation. In this paper, the photocatalytic hydrogen production over NiO/La-NaTaO₃ photocatalyst using glucose as electron donor is investigated. The H₂ production has been stable and the photo induction recombination between electron-hole has been avoided.

2. Experimental

2.1. Preparation of La-NaTaO₃

All reagents were of analytical grade and were used without further purification. Photocatalyst La-NaTaO₃ was synthesis by a sol-gel method [14]. A typical synthesis was carried out as follow: 1.5 g of tantalum chloride (TaCl₅ 99,9%) was dissolved and stirred in 150 ml ethanol (C₂H₅OH 99,9%), the stirring continuous for several hours until the solution became transparent (denoted solution A). 0,8 gram of sodium hydroxide (NaOH 99,9%) was dissolved in 50 ml distilled water and stirred for 15 minutes (denoted: solution B). Then, both solutions were mixed using magnetic stirrer (denoted: solution C). To this solution, 0,0362 grams lanthanum (La(NO₃)₃.6H₂O (99,9%)) was dissolved in 15 ml distilled water and stirred for 15 minutes then added to solution C by using pipette. Afterward, 4 g of citric acid was dissolved in 50 ml distilled water, poured into burette and introduced to the mixture by drop wise to obtain sol liquid at room temperature. The pH level was adjusted at 4 by adding NH₄OH to ionize the citric acid. The mixture was then heated and maintain at 80°C until white gel formed. The gel then was dried in the oven at 110°C and calcined at 450°C for 4 h. Lastly it was calcined at 800°C for 8 h while flowing air in the reactor to increase crystallinity[15].

2.2. Preparation of NiO

NiO co-catalyst was prepared by dissolving Ni(NO₃)₂.6H₂O in water and deposited in La-NaTaO₃ via impregnation method [16]. Nickel between 0.1 – 1.0 % wt. from Ni(NO₃)₂.6H₂O was dissolved in distilled water to mixed with 1 gram of La/NaTaO₃. The mixture stirred for 6 h at room temperature. Nickel-loaded NaTaO₃ was heated in oven at 110°C overnight, and then calcined at 300°C for 1 h to form NiO oxide.

2.3. Catalyst Characterization

There are a few characterization methods for photocatalyst such as X-Ray *diffraction* (XRD) and scanning electron microscopy (SEM) observation to study composition and morphology which contain important information. XRD measurement was conducted by using Shimadzu XRD 600 X-ray diffractometer (30 kV, 30 mA). The morphology of the prepared sample was recorded by Scanning electron microscope (SEM) using a Philips XL-30 (15 kV, 70 Pa). A prepared sample was filled through gold sputtering in the surface of La-NaTaO₃. The picture was gained through scanning electron microscope gained at 15 kV with 10000 times enlargement.

2.4. Evaluation of photocatalytic reaction

Photocatalytic reaction was carried out in Pyrex glass reactor under UV light irradiation for H₂ evolution. The reaction was performed in 500 ml reactor by taking of 350 ml distilled water containing of glucose between 0.010 - 0.125 mol L⁻¹. Before irradiation, 0.30 g of catalyst was suspended by using a magnetic stirrer and Ar gas was bubbled through the reaction mixture to remove oxygen. The irradiation source was using 400-Watt Mercury Lamp ($\lambda \geq 250$ nm). The photocatalytic activity was determined by measuring the amount of hydrogen production for 2 h irradiation. The reaction was conducted at 30°C. The amount of hydrogen measured using gas chromatography (Shimadzu GC-8A) using molecular sieve 5A column, thermal conductivity detector, and nitrogen as a carrier gas.

3. Results and discussion

3.1. Morphology

The La-NaTaO₃ photocatalyst in this research was prepared by sol-gel method and calcined at 800°C. SEM characterization was performed to the sample was meant to gain information about the morphology, shape, and size of the particle. The SEM characterization of NaTaO₃ and La-NaTaO₃ are shown in Figure 1 & 2.

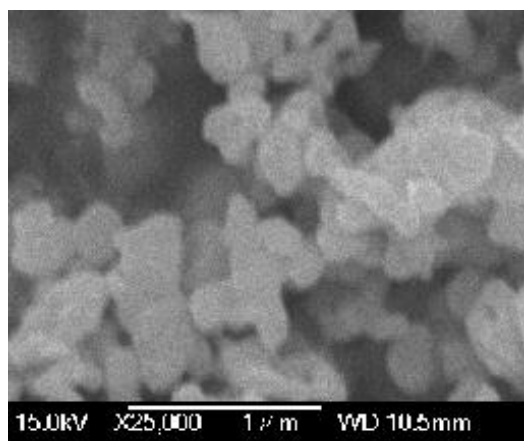


Figure 1. SEM Images of NaTaO₃.

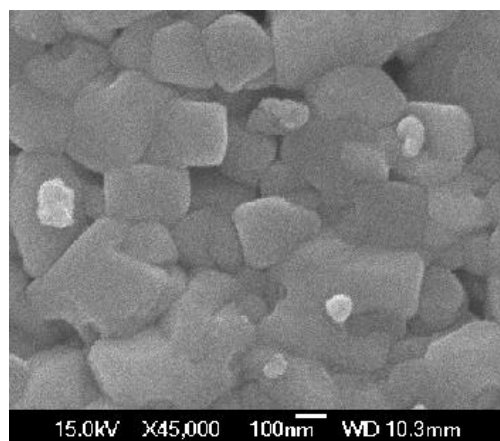


Figure 2. SEM Images of La-NaTaO₃.

From Figure 1, NaTaO₃ without lanthanum has irregular shape with agglomeration. The particle size is formed with the range of 300 – 700 nm. Figure 2 shown SEM images of LaNaTaO₃ sample. From the SEM images, an orderly-crystallized particle was formed with orthorhombic structure. The surface seems clean, with clear angle indicating the synthesized material has a high degree of crystallinity. The particle sizes of the sample were ranging between 30 – 250 nm. The result confirmed that with the addition of lanthanum, the crystallinity become well and the size become smaller. It is due to the ability of lanthanum to preserve the stability of substance avoiding the agglomeration of

synthesized particles when introduced to high temperature. The higher degree of crystallinity contributed to the photogenerated electron and hole separating efficiency and H_2 evolution enhancement. It is in accordance to the report from Husin et al. that $LaNaTaO_3$ calcined at $800^\circ C$ has orthorhombic perovskite structure with high crystallinity [15]. Calcination at high temperature is a factor in structure formation into orthorhombic crystal. Nickel particles are not seen through SEM recorded due to its small amount loading.

3.2. Crystal Structure

Figure 3 shows 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 $2\theta: 22.7^\circ$, 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 [7].

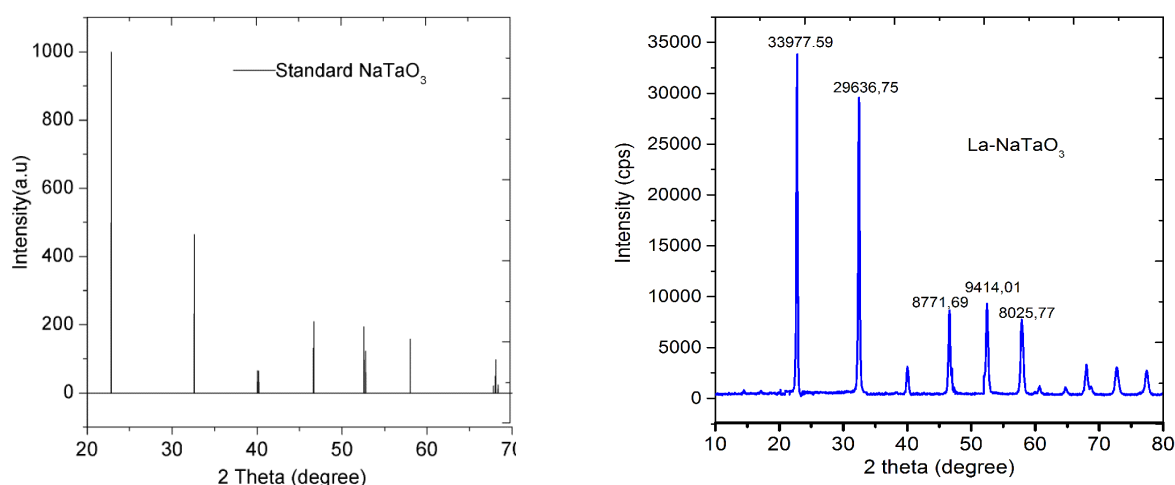


Figure 3. XRD patterns of (a) $NaTaO_3$ standard (b) $LaNaTaO_3$ sample.

3.3. Effect of glucose concentration and NiO loading

Figure 4 shows hydrogen production from water at various glucose concentrations. Without the existence of glucose, the hydrogen yield is only $0.29 \text{ mmol h}^{-1} \cdot \text{g}^{-1}$. Addition of small amount of glucose (0.01 mol L^{-1}) shows a very good improvement in hydrogen production ($1.70 \text{ mmol h}^{-1} \cdot \text{g}^{-1}$). With increasing glucose concentration up to 0.10 mol L^{-1} , an increase in the hydrogen production is observed ($5.70 \text{ mmol h}^{-1} \cdot \text{g}^{-1}$), i.e. 19.7 times higher than the non-glucose solution. It can be seen that the relation between hydrogen production rates in the presence of glucose as a sacrificial reagent are proportionally increased. When the photocatalytic reaction done with the accompany of electron donors such as glucose, photogenerated hole in the valence band irreversibly oxidized glucose instead of H_2O , thus facilitating water reduction by potential electron conduction. Further increase of glucose concentration, the hydrogen production activity is seen decreasing and this may be due to saturation of catalyst active sites.

Photocatalytic hydrogen production from glucose aqueous solution is carried out over 0.3 wt% NiO loaded $La-NaTaO_3$ photocatalysts, as can be seen in Figure 5. Hydrogen production is 0.29 on bare $La-NaTaO_3$ catalyst. The co-catalyst of NiO on $La-NaTaO_3$ from glucose aqueous solution resulted in a substantial improvement in the hydrogen evolution. In nickel loaded on $La-NaTaO_3$, the samples showed much higher photocatalytic activity from glucose water mixture compared with pure water, as

illustrated in Figure 5.

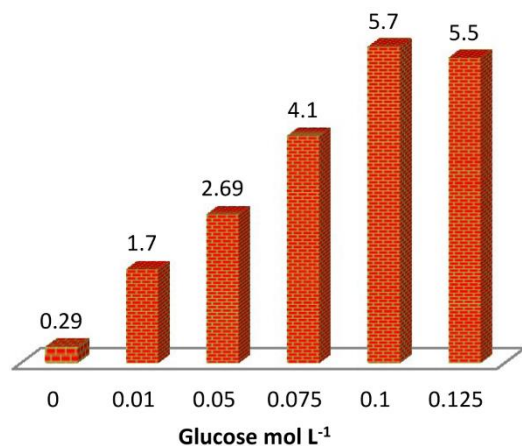


Figure 4. Effect of glucose concentration on hydrogen production without nickel loaded; Reaction condition: Glucose + water mixture of 350 ml, catalyst 0.3 g. UV light source.

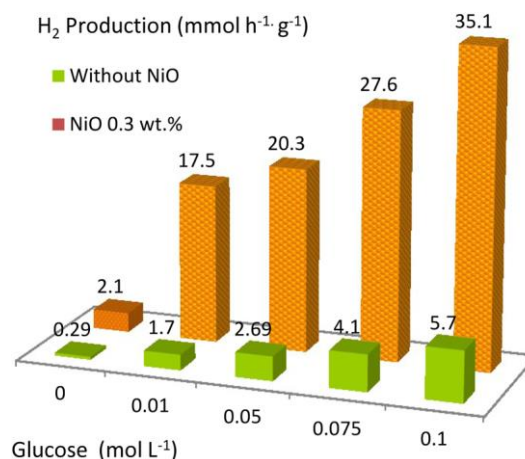


Figure 5. Effect of glucose concentration at NiO 0.3 wt.%, on hydrogen production; Reaction condition: Glucose + water mixture of 350 ml, catalyst 0.3 g. UV light source.

Figure 6 shows the hydrogen production over various NiO loaded La-NaTaO₃ photocatalysts in 0.05 mmol L⁻¹ glucose aqueous solution. The higher photocatalytic activity of nickel loaded samples with increasing NiO loading up to 0.3 wt% could be due to the improved dispersion of NiO particles over La-NaTaO₃ photocatalyst. This may be seen as that at 0.3 wt% nickel loading on La-NaTaO₃, the light harvesting as well as the lower electron hole recombination are satisfied.

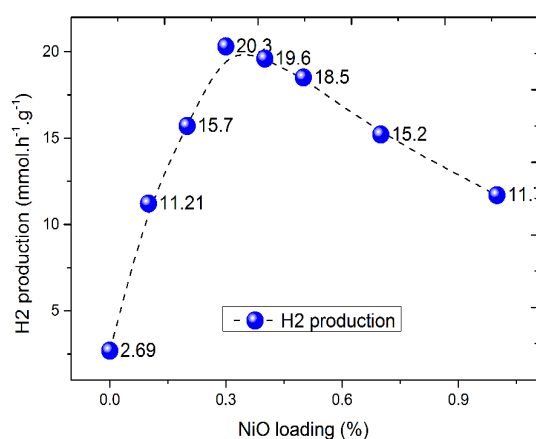


Figure 6. Effect of various NiO loading on hydrogen production; Reaction condition: Glucose + water mixture of 350 ml, 0.05 mol.L⁻¹ of glucose, 0.3 g catalyst in the solution, UV light source.

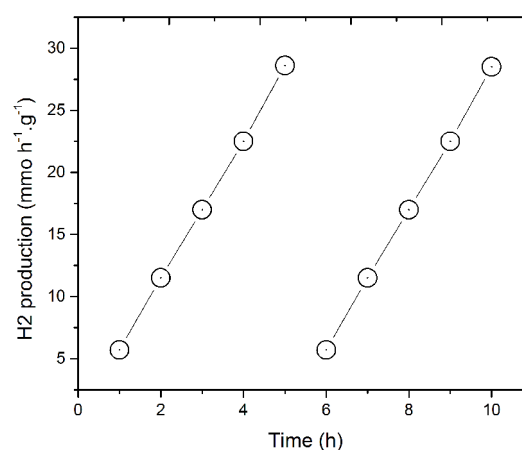


Figure 7. Hydrogen production activity; Reaction condition: reaction glucose + water mixture of 350 ml, 0.10 mol.L⁻¹ of glucose, 0.3 g in the solution, UV light source.

Co-catalyst loading is very effecting to increase photocatalytic activity at certain condition. If the amount is in the right portion then the production can be maximize [17]. The amount of co-catalyst in

the mixture are small, the active site for the process to take place are inadequate resulting low production. On the other hand, when the NiO concentration increased above 0.3 wt%, the photocatalytic activity decreased gradually. The phenomenon suggest that loading co-catalyst continuously will cover photocatalyst surface and decrease light absorbance capacity by La-NaTaO₃ semiconductor [18]. This fact explains nickel loading above 0,3% has negative result in the H₂ production[19, 20]. Nickel has probably cover the photocatalyst surface thus reducing photocatalyst effectiveness in absorbing light affecting the performance of the photocatalyst itself [21].

3.4. Photocatalytic Performance Stability

Figure 7 shown cumulative H₂ productions over La-NaTaO₃ catalyst during 5 h. Two cycles of reaction were carried out. It can be found that hydrogen evolves steadily during the reaction; no decline of activity has been detected during the span of time about 10 h. The H₂ generation rate of La-NaTaO₃ is about 5.7 mmol h⁻¹.g⁻¹, which is comparable with some photocatalysts reported before [22]. It can be concluded that the catalyst is stable enough in its performance.

4. Conclusions

NiO/LaNbTaO₃ crystall photocatalyst has been sintesized through the sol-gel method. Using glucose as electron donor, photocatalytic hydrogen generation over NiO/La-NaTaO₃ was investigated. Lanthanum has been proven to change the morphology, particle size, and crystallinity of the substance into a much suitable for the photocatalytic process. The amount of hydrogen production was found to be depending on the glucose concentration and NiO content. The optimum amount of glucose for NiO/La-NaTaO₃ was found to be about 0.10 (mol L⁻¹). Deposition with NiO particles was found to be greatly enhancing the photocatalytic activity of La-NaTaO₃.The highest activity for hydrogen evolution of 35.1 mmol h⁻¹.g⁻¹ was obtained at 0.10 mol.L⁻¹ of glucose and 0.3 wt.% of NiO. The NiO particles were oxidized and self-regulated to achieve the optimum valence for maximum activity during the course of reaction.

Acknowledgment

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