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Enhanced photocatalytic hydrogen production from water-ethanol solution by Ruthenium doped La-NaTaO₃

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Abstract. The photocatalytic hydrogen production from ethanol aqueous solution, with the use ruthenium doped La-NaTaO₃ has been investigated. Ruthenium doped La-NaTaO₃ catalysts are prepared by impregnation method. The catalysts are by X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The Ru co-catalyst demonstrated from the TEM image shows a good dispersion on the surface of La-C-NaTaO₃ with an average particle size between 4-5 nm. The photocatalytic reaction is carried out in a closed reactor with a gas circulation system. The catalytic activity of La-NaTaO₃ improved markedly (6.6 times from pure water) when Ru is loaded onto its surface. The hydrogen production is notably enhanced in the presence of ethanol as electron donors. This result is much higher when compared with the rate of hydrogen production in the sample without co-catalysts about 9.4 times higher after Ru deposition from ethanol aqueous solution. Increasing the production of hydrogen on the Ru/La-NaTaO₃ closely related to the decrease in recombination between electron-hole pairs.

1. Introduction

Hydrogen one of the main challenges facing humanity is the generation of alternative clean and renewable fuels that allowing meeting the future energy needs. Environmental pollution and energy consumption are two of the most serious issues affecting the planet and the human race at present. Moreover, the contribution of greenhouse gasses to global warming, in particular, carbon dioxide emissions is driving the urgent development of clean, sustainable energy sources. About 85% of our energy consumption is provided by fossil fuels, which will not be able to keep up with the increasing energy demand [1-3].

One promising approach to alleviate the energy crisis is the use of hydrogen from water and light, due to it is environmentally friendly energy sources [4, 5]. Photocatalytic water splitting represents one of the promising technologies for clean and environmentally friendly hydrogen production and provides a way to use sunlight for generating hydrogen as a renewable green fuel. The photocatalytic process is initiated by the absorption of a photon with energy equal to or larger than the band gap of the semiconductor. The photoexcited carriers separate and migrate to the surface without recombination, and adsorbed species are reduced and oxidized by the photogenerated electrons and holes to produce H₂ and O₂ [6-8].



However, photogenerated electrons are also very easy to recombine of photo-generated electron/hole pairs in the semiconductor and the fast backward reaction of hydrogen and oxygen to form water. Thus, RuO_2 as co-catalyst can help push electron transfers and enhance photocatalytic activity [9, 10]. Although the loading with a co-catalyst can reduce the charge carrier recombination to some extent, hydrogen production from pure water splitting is difficult to achieve since the recombination of the electron-hole pairs cannot be completely eliminated. Some works reported in the last decades have shown that it was possible to increase the hydrogen production reaction rate using water-methanol systems. Therefore, electron donors as well as other mediators are usually required to avoid this problem. Regarding the photocatalytic of H_2 production, different substances e.g., methanol, EDTA, sulphide, acting as electron donors, have been generally used in many studies [11-13]. Ethanol is regarded as a credible and important source for H_2 production because of its can act as electron donor for the photocatalytic H_2 production on semiconductor, in comparison, its rarely being employed and a renewable nature.

Based on the above background, the aim of the present work is to study the influence of Ru as co-catalyst and ethanol as sacrificial reagents on photocatalytic water splitting reactions to produce of hydrogen under ultraviolet (UV) irradiation. An attempt was made to synthesis of RuO_2 deposited on La-NaTaO_3 at ambient temperature by inception wetness method. The obtained RuO_2 deposited on La-NaTaO_3 shown excellent properties photocatalysts.

2. Materials and methods

2.1. Chemical reagents

In this work, tantalum chloride (TaCl_5 , 99.9%): Acros organics), sodium hydroxide (NaOH , 99.9%: Acros organics), $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Acros Organics; 99.9%), anhydrous citric acid ($\text{C}_6\text{H}_8\text{O}_7$, 99.5%: Merck), ammonia (NH_4OH , 35%: Fisher Scientific, ethanol ($\text{C}_2\text{H}_5\text{OH}$, 99.5% Merck) was used as precursor for the synthesis of La-NaTaO_3 . Triruthenium dodecarbonyl ($\text{Ru}_3(\text{CO})_{12}$, Aldrich, 99%) were used for the synthesis of RuO_2 . Deionized water was used in whole experiments. Argon gas (Ar :99.99%), and nitrogen gas (N_2 : 99.99%) were used in calcination process. All gases were purchased from Serikat Company Banda Aceh, Indonesia.

2.2. Synthesis of $\text{RuO}_2/\text{La-NaTaO}_3$ nanocrystalline

All the reagents with analytical grade were used without further purification. La-NaTaO_3 was synthesized by a sol-gel method as previously reported by our group elsewhere [14]. In a typical preparation of TaCl_5 was dissolved in excess ethanol solution under vigorous stirring. A required amount of NaOH was slowly added into the TaCl_5 solution followed by vigorous stirring for 1 h. $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ was dissolved separately in 15 ml deionized water and the solution containing $\text{La}(\text{NO}_3)_3$ added dropwise into the above solution. Citric acid was dissolved in 50 ml of deionized water and then dropwise into the above solution by stirring for 2 h to produce a transparent sol. The pH of the solution was adjusted to 4 by adding an ammonia solution to ionize the citric acid. The transparent solution was then heated at temperature of 90 °C, followed by stirring to obtain white gels. The obtained gels were poured into crucible porcelain and dried in oven at 110 °C during 7 h. The resulting samples was crushed and then pre-heated at 450 °C for 4 h in muffle furnace. The powder was continued calcination at temperature of 800 °C in air for 8 h. Finally, the resulting powder was crush by mortar and characterized by several methods.

Loading ruthenium oxide as active phase onto the obtained La-NaTaO_3 was performed by an impregnation method with a $\text{Ru}_3(\text{CO})_{12}$ (Aldrich, 99%). Typically, 1.0 g of La-NaTaO_3 was first filled in beaker glass. Triruthenium dodecarbonyl ($\text{Ru}_3(\text{CO})_{12}$) was dissolved in distilled water and then mixed with La-NaTaO_3 powder. The samples were mixed by stirring at atmospheric pressure and room temperature for 6 h. Thereafter, the slurry was dried at 110 °C overnight. The obtained sample was further oxidized in flowing air (100 mL/min at 300 °C for 3 h) to form RuO_2 .

2.3. Characterization of nanocrystalline

The morphology of the powders was inspected by a scanning electron microscope (JEOL 5600 SEM). HRTEM images were obtained by a JEOL Model JEM 2010 EX instrument at an accelerating voltage of 200 kV. X-ray diffraction patterns (XRD) of tantalates were obtained with a Shimadzu 7500 X-ray advanced diffractometer with a Cu-K α radiation ($\lambda = 1.5406 \text{ \AA}$). The accelerating voltage and the applied current were 40 kV and 40 mA, respectively. The phases present in the samples were identified with the help of JCPDS (Joint Committee of the Powder Diffraction Standard) database files.

2.4. Photocatalytic hydrogen generation

The photocatalytic reaction of hydrogen production from water-ethanol solution was carried out in a Pyrex closed gas circulation reactor. In a typical experiment, 0.3 g of the photocatalyst (Ru/La-NaTaO₃) was suspended in 350 ml ethanol water mixture (of 10 vol.% aqueous ethanol solution). A 400 W Mercury Lamp was used as a light source irradiated inside of the reactor. Before irradiation, the quartz flask was then connected to the experimental set-up and Ar gas was bubbled through the reaction mixture for 30 min to remove dissolved oxygen. The reactor temperature was maintained at 25 °C by means of a cooling fan. The hydrogen evolution was collected by collector gas. The hydrogen evolution rate was measured at room temperature under atmospheric pressure. Gas samples were analyzed using a thermal conductivity detector (TCD) gas chromatograph (Shimadzu, GC-8A).

3. Results and discussion

3.1. Surface morphology

The morphology of the synthesized catalysts was analyzed by scanning electron microscopy (SEM) and high resolutions (HR-SEM). Figure 1 shows SEM images of the RuO₂/La-NaTaO₃ catalysts. It can be seen in Figure 1, the RuO₂/La-NaTaO₃ catalyst are quite homogeneous nano-sized particles.

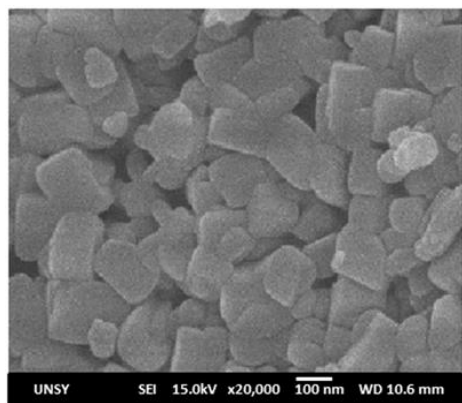


Figure 1. SEM image of RuO₂/La-NaTaO₃ photocatalyst.

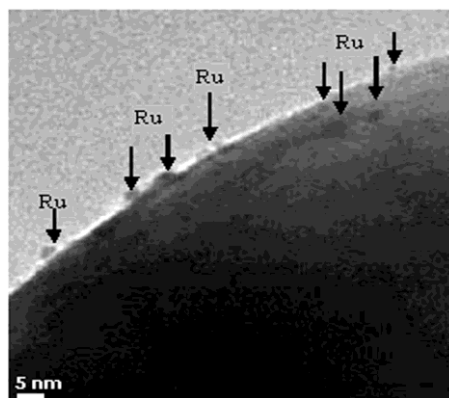


Figure 2. HRTEM image of RuO₂ oxide on La-NaTaO₃ surface.

All La-NaTaO₃ particles have similar morphologies of orthorhombic shape NaTaO₃. There is no serious aggregation of nanocrystalline. As demonstrated in Figure 1, all of the photocatalyst particles are very small with sizes of 50 - 150 nm, which is much smaller than the particle sizes synthesized by traditional solid state reaction method, indicating that sol-gel method can effectively inhibit the agglomeration of the NaTaO₃ nanoparticles. This morphology is typically observed for well-prepared nanocrystalline reported in the literature [15]. High crystallinity of the particles, for La-NaTaO₃, was confirmed by TEM analyses, showing smooth surface of the particles (Figure 1).

To further study the effect of the ruthenium content on the surface catalyst, several catalysts were prepared by deposition of Ru via inception wetness. The morphology and dispersion of Ru deposited

particles on La-NaTaO₃ were also confirmed by high resolution transmission electron microscopy. A representative TEM image of 0.6 wt.% RuO₂ is illustrated in Figure 2. It is clearly seen that Ru oxide particles in the range of 4 - 5 nm were well dispersed on the surface of La-NaTaO₃ with no aggregation. The size distribution of ruthenium particles is fairly uniform.

3.2. Crystal structure and composition

The crystal structure of RuO₂/La-NaTaO₃ was analysed by X-ray diffractometer (XRD). Figure 3 shows XRD patterns for the RuO₂/La-NaTaO₃ catalysts. The XRD spectra of RuO₂/La-NaTaO₃ in Figure 3 reveal that the RuO₂/La-NaTaO₃ photocatalysts had a crystal structure that was identical to that of the un-doped NaTaO₃. The peaks at $2\theta = 22.73, 32.54, 52.72^\circ$ can be assigned to the diffraction pattern of pure NaTaO₃ of orthorhombic structure. As depicted in Figure 3, high crystallinity of the particles was confirmed by XRD analyses, showing narrow peaks, which could effectively inhibit the recombination of photogenerated carriers [16]. Loading a small amount of ruthenium and doping of lanthanum confirming that no crystalline phase involving ruthenium oxides and lanthanum oxides was recorded.

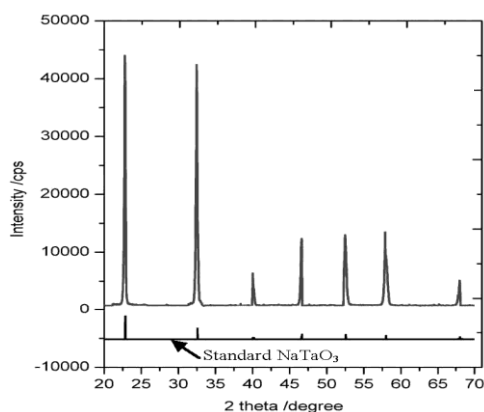


Figure 3. X-ray diffraction patterns of RuO₂/La-NaTaO₃ photocatalyst.

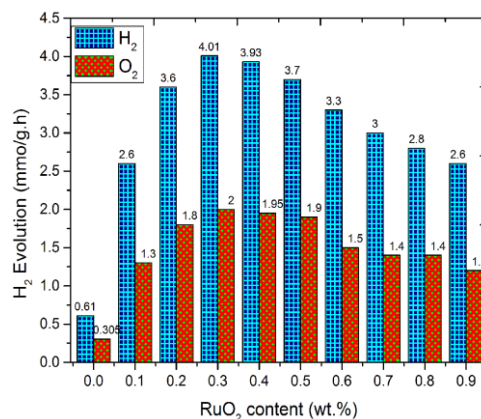


Figure 4. Formation rate of H₂ and O₂ as a function of RuO₂ content on La-NaTaO₃ from pure water (350 ml solution and 3 g catalyst).

3.3. Photocatalytic activities

The photocatalytic hydrogen evolution over the RuO₂/La-NaTaO₃ catalysts from water splitting as a function of ruthenium loading is displayed in Figure 4. The experiments were conducted using reactant solution of 350 ml of pure water. In a typical reaction, the catalyst powder (0.3 g, containing Ru: 0.0 - 0.9 wt.%) was suspended into the inner irradiation cell made of quartz under UV-light (400W high-pressure Hg lamp), and operated in the atmospheric and constant temperature of 25 °C. It can be seen that the bare La-NaTaO₃ exhibit very low hydrogen evolution (0.61 mmole.h⁻¹.g⁻¹). The amount of O₂ generated was approximately half as that of H₂. A significant increase in the hydrogen evolution is observed when the addition amounts of Ru as H₂ evolution site. The rate of hydrogen formation on RuO₂/La-NaTaO₃ samples is 6.6 times much higher than that obtained with the pure La-NaTaO₃. As can be seen in Figure 4, the photoactivity of RuO₂/La-NaTaO₃ increased with enhancing the RuO₂ loading from 0.1 wt.%, and reaches a maximum H₂ evolution rate (4.01 mole.g⁻¹.h⁻¹) at 0.3 wt.%. While it exceeds 0.3 wt.%, the H₂ evolution rate begins to decrease, in line with recent literature results [17]. The benefit of RuO₂ deposition is due to the capability of these metals to trap electrons. It can be considered that the enhanced photocatalytic activity by co-catalysts may be possible from the interaction between RuO₂ and La-NaTaO₃ to increase the transfer of photogenerated carriers [18] [19]. On the other hand, the excessive Ru loading will mask the La-NaTaO₃ surface, reducing the photoexcitation capacity of the La-NaTaO₃ photocatalyst [18,19].

The same trend also demonstrated in Figure 5 that the amount of hydrogen evolution increases significantly when introducing the ethanol (10 vol.%) in the solution as sacrificial reagent. In these cases, the rate of hydrogen production was found to be much higher, compared to that obtained from photocatalytic of pure water. In fact, ethanol, are not only additional proton sources, but also efficient hole scavengers which undergo fast and irreversible oxidation, thus making photo-promoted electrons more readily available for proton reduction to hydrogen [20].

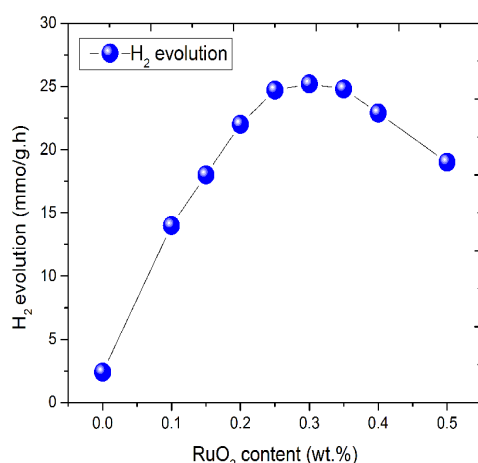


Figure 5. H₂ evolution as a function of RuO₂ content on La-NaTaO₃ from aqueous ethanol solution (350 ml, containing 10 vol.% ethanol).

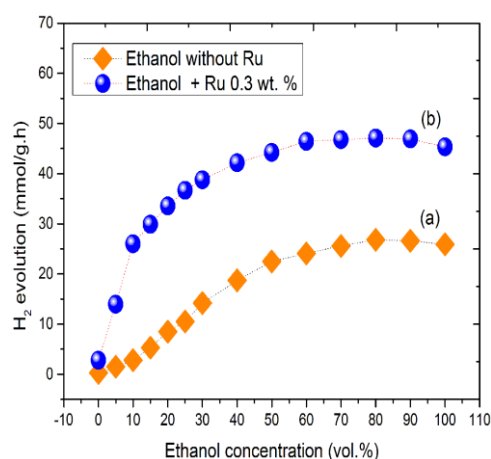


Figure 6. H₂ evolution from different amount of ethanol on La-NaTaO₃ (a) without RuO₂ (b) with RuO₂.

This fact can be explained if the ethanol acts as sacrificial electron donor and consumes photogenerated holes and/or oxygen to produce protons (H⁺) in the valence band, while Ru traps the electron from the surface to suppress the electron-hole recombination on the semiconductor's surface [4]. Similar report have studied hydrogen generation with Rh deposited on carbon and RuO₂/NaTaO₃ and its application in hydrogen production and petrochemical, proven that oxidation of ruthenium oxide occurred during reaction induced high hydrogen generation activity [21, 22].

Figure 6 shows the changes in the photocatalytic activity for H₂ production with the addition amount of ethanol over La-NaTaO₃ and RuO₂/La-NaTaO₃ suspension. The amount of H₂ production on La-NaTaO₃ at ethanol of 10% was 2.8 mmole.h⁻¹.g⁻¹ (see Figure 6.a), and reached 26.4 mmole.h⁻¹.g⁻¹ when RuO₂ introducing on La-NaTaO₃ (Figure 6.b). The increase of hydrogen production rate was about 9.4 times higher than that of in the absence of RuO₂ on the surface of La-NaTaO₃. It is observed that, combination of La:NaTaO₃ with RuO₂ gives the highest hydrogen production rate.

The effect of ethanol concentration on the photocatalytic hydrogen production at 0.3 wt.% ruthenium loading was also observed. It is demonstrated that the rate of hydrogen evolution over La-NaTaO₃ initially was 2.79 mmole.h⁻¹.g⁻¹, then increase of 13.5 mmole.h⁻¹.g⁻¹ when introducing the ethanol of 5%, and goes through a maximum at ethanol of 80%, which reaches a value of about 47.1 mmole.h⁻¹.g⁻¹. When the ethanol concentration exceeds 80%, the hydrogen evolution decreased and then tended to saturation. In this regard, the co-catalyst and ethanol plays a very important role for hydrogen evolution rate, because RuO₂ is able to capture electrons and decrease the over potential of H⁺/H, and the effect of added ethanol, which acts as sacrificial electron donor, consumes photogenerated holes and/or oxygen, leading to the decrease of the electron-hole recombination. These phenomena are in agreement with reported by other group, who reported the photocatalytic of hydrogen rate from methanol and ethanol aqueous solution [23-25].

4. Conclusions

The photocatalytic hydrogen production over RuO₂/La-NaTaO₃ nanoparticles has been studied using ethanol as a sacrificial reagent. The deposition with RuO₂ particles was found to greatly enhance the photocatalytic activity of La-NaTaO₃ toward hydrogen production from aqueous ethanol solution. The addition of an appropriate amount of ethanol to the reactant solution was shown to enhance H₂ evolution, which is very important to practical application. RuO₂ is able to capture electrons and decrease the over potential of H⁺/H, and ethanol acting as an electron donor to scavenge photoinduced holes quickly so that the recombination of photoinduced electrons and holes at the RuO₂/La-NaTaO₃ surface are inhibited.

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