

# Photocatalytic Hydrogen Production over Ni/La-NaTaO<sub>3</sub> Nanoparticles from NaCl-water Solution in the Presence of Glucose as Electron Donor

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Nanoparticles La-NaTaO<sub>3</sub> photocatalyst has been synthesized via a sol-gel route. A Ni nanoparticle (NPs) as a cocatalyst is loaded on La-NaTaO<sub>3</sub> by a simple impregnation method. The products are characterized by X-ray diffraction (XRD), scanning electron microscope (SEM), a high-resolution transmission electron microscope (HRTEM) and X-ray photoelectron spectroscopy (XPS). X-ray diffraction of the La-NaTaO<sub>3</sub> samples shows perovskite-type crystalline orthorhombic structure. Small particulate solids of La-NaTaO<sub>3</sub> (30-250 nm) are observed by SEM measurement. The nickel particles are detected from HRTEM images is around 4-8 nm. The hydrogen evolution over La-NaTaO<sub>3</sub> with NaCl is much higher than that without NaCl. The photoactivity of La-NaTaO<sub>3</sub> is enhanced when Ni is loaded on the surface of La-NaTaO<sub>3</sub>. The optimum loading amount of nickel is found to be 0.3 wt.% for La-NaTaO<sub>3</sub>, and it is more effective for H<sub>2</sub> production from NaCl-water solution in the presence glucose. It is revealed that the loaded Ni can interact with each other and cooperate on improving the photocatalytic activity. In the case of glucose as an electron donor, the activity of photocatalytic hydrogen generation over Ni/La-NaTaO<sub>3</sub> increases dramatically. NaCl and glucose can promote markedly the photocatalytic hydrogen evolution. The Ni/La-NaTaO<sub>3</sub> nanoparticles system appears to be a promising candidate, which is very important to practical applications, including the production of H<sub>2</sub> from NaCl-water solution in the presence of glucose.

**Keywords:** La-doped sodium tantalum oxide; Nickel; Photocatalyst; Glucose; Hydrogen energy

## INTRODUCTION

Hydrogen production technology has been considered as one of the most

important topic studied due to its potential application. At present time, hydrogen is mainly produced by the reforming process at high temperature of light hydrocarbons.

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Due to highly endothermic nature of steam reforming reactions, a significant amount of energy needs to be supplied. Thus, development of an alternative hydrogen production method is absolutely imperative to mitigate the environmental and energy issues. Photocatalytic water splitting (PWS) is one of the most promising ways for production of hydrogen from water (Muradov and Veziroğlu, 2008; Husin *et al.*, 2014a).

About 97% of the earth's water is salty, while less than 3% is fresh water (Li *et al.*, 2011; Shinde *et al.*, 2011). H<sub>2</sub> can be obtained from seawater by electrolysis. Unfortunately, this method is disadvantageous because of low efficiency and high cost (Ji *et al.*, 2007). Almost all studies on PWS so far have been performed in pure water. From the viewpoint of practical application, producing hydrogen from NaCl solution, a major component of seawater, would be highly desirable. However, few studies on the hydrogen production from salt have been made. Maeda *et al.* have investigated effects of some electrolytes including NaCl on the photocatalytic activity of (Ga<sub>1-x</sub>Zn<sub>x</sub>)(N<sub>1-x</sub>O<sub>x</sub>) for overall water splitting under visible light (Maeda *et al.*, 2009; Husin *et al.*, 2015). Ji *et al.* reported PWS from seawater over La under ultraviolet light, and over CdS/TiO<sub>2</sub> under visible light (Ji *et al.*, 2007).

In the absence of an electron donor, the efficiency of photocatalytic hydrogen generation over a semiconductor photocatalyst is very low due to the recombination of photo-induced electrons and holes on the semiconductor surface. To resolve this problem, electron donors (sacrificial reagents or hole scavengers,

such as methanol, Na<sub>2</sub>S, Na<sub>2</sub>SO<sub>3</sub>, and glucose) were added to react irreversibly with the photogenerated VB holes ( $h^+$ ), thereby suppressing the electron-hole recombination (Chowdhury *et al.*, 2015). Glucose is believed to be one of most suitable sacrificial agents, since it can be synthesized from biomass and utilized for the sustainable production of hydrogen (Fu *et al.*, 2010). Glucose is a cheap electron donor, taken as a representative of biomass in this work. Our group has reported that the enhanced photocatalytic H<sub>2</sub> production over La-NaTaO<sub>3</sub> from aqueous methanol solution (Husin *et al.*, 2014b). To the best of our knowledge, there is no research focused on the photocatalytic hydrogen production from NaCl-water solution over La-NaTaO<sub>3</sub>.

The aim of the present work was to investigate the effects of electrolyte NaCl on photocatalytic hydrogen evolution in the presence of glucose as electron donor over Ni/La-NaTaO<sub>3</sub>. The optimal loading amount of nickel was also discussed for fundamental understanding of the photocatalytic performance. Further investigation on photocatalytic hydrogen evolution over Ni/La-NaTaO<sub>3</sub> from natural seawater is under progress.

## MATERIALS AND METHODS

### Chemical Reagents

Analytical grade tantalum chloride (Acros, 99.9%), sodium hydroxide (Acros, ACS grade), ethanol (Acros, 99.5%), lanthanum nitrate (Merck, 98.0%), citric acid (Acros, 99.0%), ammonium solution (35% Fisher Scientific), Ni(NO<sub>3</sub>).6H<sub>2</sub>O (Acros Organics; 99.0%), ethanol, and glucose (Merck, 98.0%) were used without further

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purification. All solutions were prepared using high-purity deionised water from local sources. Argon (Ar) and N<sub>2</sub> gas were used for purging and as GC carrier, respectively. All gases were purchased from Serikat Company Banda Aceh, Indonesia.

### Preparation of Ni/La-NaTaO<sub>3</sub>

The synthesis of La-doped NaTaO<sub>3</sub> is in accordance to the procedure for the preparation of pure nanocrystalline NaTaO<sub>3</sub> reported previously (Husin *et al.*, 2014b). A typical synthesis was carried out as follows: TaCl<sub>5</sub> was dissolved in 50 ml of ethanol. NaOH was then dissolved in deionised water in the presence of excess amounts (5-6%) of alkali to compensate the volatilization. The solutions were mixed with magnetic stirring. To this solution, 2.0 mol.% anhydrous La(NO<sub>3</sub>)<sub>3</sub>.6H<sub>2</sub>O was added with vigorous stirring and then added into the solution with citric acid being used as a chelating agent. The pH was controlled at 4 by NH<sub>4</sub>OH solution. The resulting sol solution was then heated and the temperature was kept constant at 80 °C until white gels were formed. The resulting products were dried in oven at 110 °C, followed by calcinations at 400 °C for 4 h. The powders were well mixed by grinding, followed by calcination at 800 °C for 8 h.

La-doped NaTaO<sub>3</sub> was used as photocatalyst to prepare a series of Ni/LaNaTaO<sub>3</sub> catalysts with varying Ni loadings according to the wet impregnation method. Appropriate amounts of Ni(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O (0.1, 0.2, 0.3, 0.4 and 0.5 wt.%, respectively) were dissolved in 5 mL of distilled water. Each aqueous solution of Ni(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O was slowly added to 1 g of the La-doped NaTaO<sub>3</sub>

photocatalyst. The resulting slurry was then stirred at ambient for 5 h. After impregnation, the catalysts were dried at 105 °C overnight and then calcined at 300 °C for 1 h in air at a heating rate of 0.5 °C/min. Ni/LaNaTaO<sub>3</sub> was reduced in H<sub>2</sub> atmosphere at 500 °C for 2 h to obtain Ni metal.

### Characterization of Ni/La-NaTaO<sub>3</sub>

The powder X-ray diffraction (XRD) pattern for the synthesized nanocatalyst samples were recorded on a Shimadzu 7500 X-ray diffractometer with a Cu K $\alpha$  source, wavelength,  $\lambda = 0.15406$  nm. To observe particle morphology, scanning electron micrographs (SEM) were taken using a JEOL 7000F operating at 15 kV, while transition electron microscopy (TEM) was conducted using a JEOL 2100 Cryo operating at 200 kV. Surface analysis was conducted by XPS using a KRATOS XSAM-800 model with an operating base pressure of ca. 10<sup>-9</sup> Torr. The X-rays, from Al K $\alpha$  ( $h\nu = 1486.6$  eV) radiation, were used at 180 W. Collection of spectra was performed at a pass energy of 20 eV.

### Evaluation of Photocatalytic Activity of Ni/La-NaTaO<sub>3</sub>

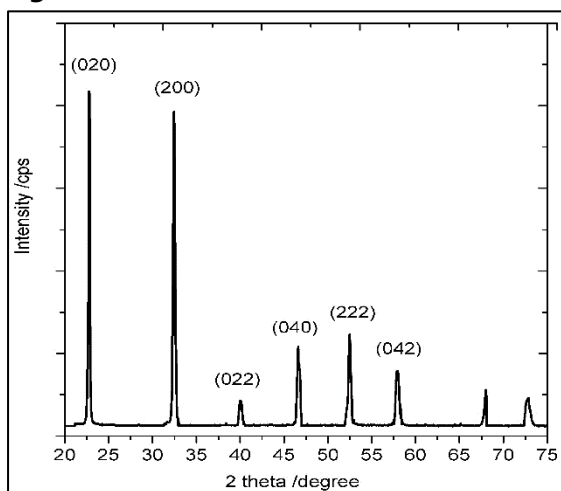
Photocatalytic hydrogen production was performed at room temperature under atmospheric pressure in a closed circulation system. In all experiments, 350 ml 10 vol.% aqueous glucose (0.1 mol.L<sup>-1</sup>) containing 0.3 g catalyst was added into the cell and a given concentration of NaCl. A 400W Hg lamp was used as the light source. Prior to irradiation, the air inside the reactor was purged by Ar gas. The concentration of H<sub>2</sub> was analyzed by gas

chromatography Shimadzu 8A, with a thermal conductivity detector (molecular sieve 5 Å column and N<sub>2</sub> carrier).

## RESULTS AND DISCUSSION

### Crystal Structure and Composition

All samples exhibited characteristic peaks around  $2\theta = 22.73, 32.54, 52.72^\circ$  that can be assigned to the diffraction pattern of NaTaO<sub>3</sub>. The XRD patterns of Ni/La-NaTaO<sub>3</sub> oxide nanocatalyst show the formation of pure NaTaO<sub>3</sub> orthorhombic structure (JCPDS card no. 25-0863, space group Pcmn) phases clearly, as shown in **Figure 1**.

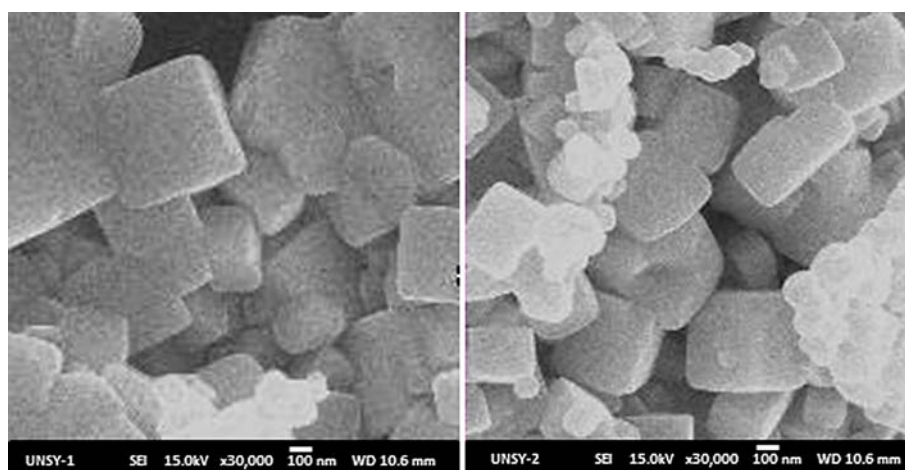


**Fig. 1:** XRD patterns of Ni/La-NaTaO<sub>3</sub> photocatalyst

The patterns exhibit the formed metal oxide catalyst without any impurity phase, suggesting that nanoparticle having higher crystallinity. High crystallinity is expected to prevent recombination between electrons and holes, thus increasing the efficiency of photocatalytic hydrogen production. Similar examples have been documented in the literature, such as the effect of doping on NaTaO<sub>3</sub> and TiO<sub>2</sub> and their photocatalytic activity (Husin *et al.*, 2014b; Yang *et al.*, 2015).

The average size of the Ni/La-NaTaO<sub>3</sub> orthorhombic particle calculated by Debye-Scherrer formula was 25-46 nm. On the other hand, no XRD peaks for Ni was observed for catalysts loaded with 0.5 wt.% nickel, indicating good dispersion of the very small Ni particles. This is possibly due to the low loading, and the deposition of nickel onto the surface of LaNaTaO<sub>3</sub> 0.1-0.5 wt.%.

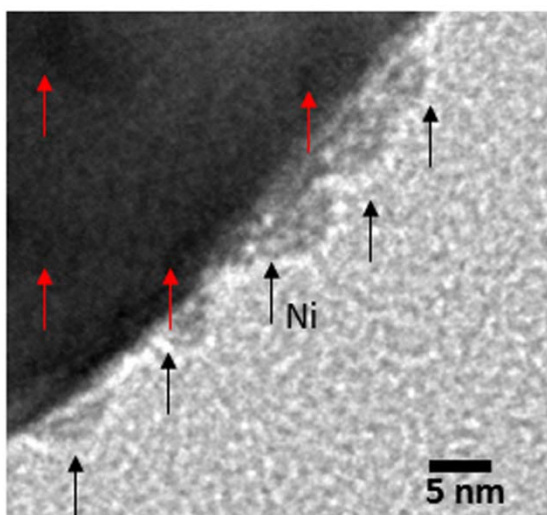
The morphology of the synthesized catalysts was analyzed by FE-SEM, as depicted in Figure 2. All samples have similar morphologies of orthorhombic shape NaTaO<sub>3</sub>. Our results are in agreement with La-doped NaTaO<sub>3</sub> system previously



**Fig. 2:** SEM image of Ni/La-NaTaO<sub>3</sub> photocatalyst

reported by other group (solid state and microwave process), who also observed an orthorhombic perovskite structure (Kato *et al.*, 2003; Yan *et al.*, 2009). There is no serious aggregation of nanocrystalline. As demonstrated in Figure 2, the morphology of the La-NaTaO<sub>3</sub> sample was well-developed with a particle size around 30-250 nm, which is much smaller than the NaTaO<sub>3</sub> particles, indicating that La-doping can effectively inhibit the agglomeration of the NaTaO<sub>3</sub> nanoparticles. This morphology is typically observed for well-prepared nanocrystalline reported in the literature (Husin *et al.*, 2014a).

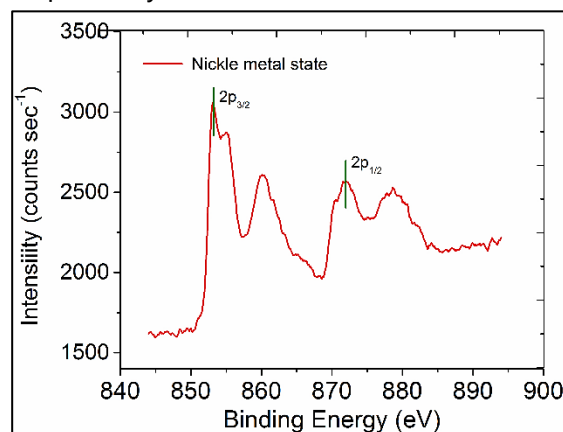
To further investigate the Ni deposition, the morphology and dispersion of Ni deposited metal particles on La-NaTaO<sub>3</sub> were also confirmed by transmission electron microscopy and X-ray photoelectron spectroscopy spectra. A representative TEM image of 0.5 wt.% Ni/La-NaTaO<sub>3</sub> is shown in **Figure 3**.



**Fig. 3:** HRTEM image of Ni metals on Ni/La-NaTaO<sub>3</sub>

The TEM images reveal that Ni particles are in the range of 4 - 8 nm. The Ni metal particles were dispersed on the surface of La-NaTaO<sub>3</sub>. There is no aggregation of nickel metals on the surface of La-NaTaO<sub>3</sub>.

The surface chemical state of Ni/La-NaTaO<sub>3</sub> was analysed by X-ray photoelectron spectroscopy. The XPS spectra of Ni/La-NaTaO<sub>3</sub> shown in Figure 4 reveal the chemical states of nickel on the surface of La-NaTaO<sub>3</sub>. The binding energy peaks for as-prepared Ni/La-NaTaO<sub>3</sub> in **Figure 4** at 852.9 and 871.6 eV correspond to metallic nickel 2p<sub>3/2</sub> and 2p<sub>1/2</sub>, respectively.

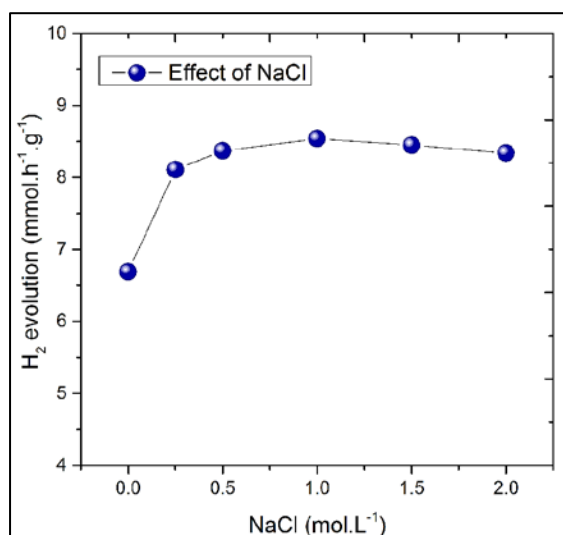


**Fig. 4:** Ni 2p XPS spectra of Ni metals on Ni/La-NaTaO<sub>3</sub>

### Photocatalytic Activities

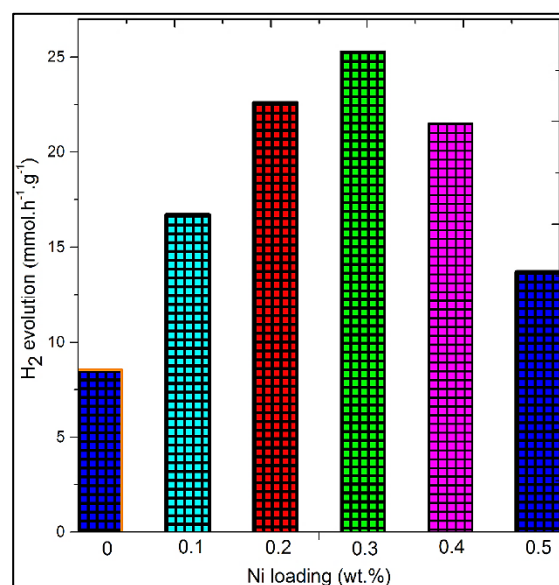
The experiments were conducted using reactant solution: 350 ml, containing 10 vol.% glucose (0.1 mol.L<sup>-1</sup>), NaCl: 0.0, 0.25, 0.5, 1.0, 1.5, and 2.0 mol.L<sup>-1</sup>, in the constant temperature of 25 °C. In a typical reaction, the catalyst powder (0.3 g) was loaded into the inner irradiation cell made of quartz under UV-light (400W high-pressure Hg lamp).

**Figure 5** shows the changes in the photocatalytic activity for H<sub>2</sub> production with the addition amount of NaCl over La-NaTaO<sub>3</sub> suspension. Under UV light irradiation, the activity increases with increasing NaCl concentration. It is observed that the rate of hydrogen evolution over La-NaTaO<sub>3</sub> initially increases with NaCl and goes through a maximum of 8.54 mol.h<sup>-1</sup>.g<sup>-1</sup> at 1.0 mol.L<sup>-1</sup> NaCl. The highest hydrogen production rate was about 1.3 times higher than that of in the absence of NaCl in the suspension. As the NaCl concentration increased the maximum H<sub>2</sub> evolution increased and then tented to saturation. This is because Na<sup>+</sup> adsorbed on La-NaTaO<sub>3</sub> promoted the adsorption of glucose. This phenomenon reported by Maeda *et al.*, that electrolyte NaCl can improve the activity markedly (Maeda *et al.*, 2009). However, further increase in NaCl concentration reduced the H<sub>2</sub> evolution rate due to the negative effect of Cl<sup>-</sup> ions.



**Fig. 5:** Photocatalytic H<sub>2</sub> evolution over La-NaTaO<sub>3</sub> photocatalyst, at various amounts of NaCl concentration, containing 10 vol.% glucose (0.1 mol.L<sup>-1</sup>)

Figure 6 shows the effect of amount of Ni loading on the photocatalytic activity. A significant increase in the hydrogen evolution is observed when the addition amounts of Ni were enhanced from 0.1 to 0.5 wt.%. As can be seen, the photoactivity of Ni/La-NaTaO<sub>3</sub> increased with enhancing the Ni loading from 0.1 wt%, and reaches a maximum H<sub>2</sub> evolution rate (25.4 mol.h<sup>-1</sup>.g<sup>-1</sup>) at 0.3 wt.%.



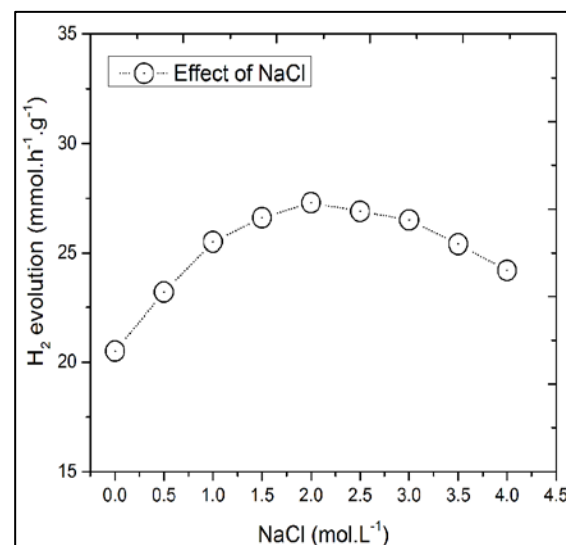
**Fig. 6:** Average H<sub>2</sub> evolution rate of La-NaTaO<sub>3</sub> at various amounts of Ni loading levels, containing 1.0 mol.L<sup>-1</sup> of NaCl and 10 vol.% glucose (0.1 mol.L<sup>-1</sup>)

While it exceeds 0.3 wt.%, the H<sub>2</sub> evolution rate begins to decrease. The benefit of Ni metal deposition is due to the capability of these metals to trap electrons (Chen *et al.*, 2015). This fact can be explained if the glucose acts as sacrificial electron donor and consumes photogenerated holes and/or oxygen to produce protons (H<sup>+</sup>) in the valence band, while Ni traps the electron from the surface to suppress the electron-hole recombination on the semiconductor's

surface (Husin *et al.*, 2013). On the other hand, the excessive Ni loading will result in the growth and agglomeration of nickel nanoparticles on the La-NaTaO<sub>3</sub> surface. It is presumed that excessive nickel loading can mask the La-NaTaO<sub>3</sub> surface, reducing the photoexcitation capacity of the La-NaTaO<sub>3</sub> photocatalyst (Husin *et al.*, 2011).

The effect of NaCl concentration on the photocatalytic hydrogen production at 0.3 wt.% nickel loading in the presence of glucose was also observed. **Figure 7** shows H<sub>2</sub> evolution for solutions of 10 vol.% glucose at different NaCl concentration. The rates of H<sub>2</sub> evolution increased with NaCl concentration to a maximum at 2.0 mol. L<sup>-1</sup>. When Na<sup>+</sup> ions are adsorbed on Ni/La-NaTaO<sub>3</sub>, relative concentration of Na<sup>+</sup> on Ni/La-NaTaO<sub>3</sub> would increase. This would result in enhancement of the interaction between adsorbed Na<sup>+</sup> and glucose to combine photoinduced holes and hydroxyl radicals quickly. It is presumably that the factor of the higher H<sub>2</sub> evolution rate at NaCl ≤ 2.0 mol L<sup>-1</sup>. Whereas when NaCl concentration more than 2.0 mol L<sup>-1</sup>, the H<sub>2</sub> evolution rates began to decrease gradually. This result was in agreement with reported by other group, who reported the activity of Pt/Cd<sub>0.05</sub>Zn<sub>0.5</sub>S with NaCl and without NaCl (Li *et al.* 2011). Similar to Pt/TiO<sub>2</sub> system, when increasing NaCl concentration, hydration of C<sub>5</sub>H<sub>11</sub>O<sub>6</sub><sup>-1</sup> (glucose ion) decreases. As a result, at high NaCl concentration more glucose ion being adsorbed in the surface catalyst (Li *et al.*, 2013). This suggests that glucose ion can compete with the surface hydroxyl group at the active sites of the catalyst. Its formation may, thus be the reason behind its

unexpectedly low activity.



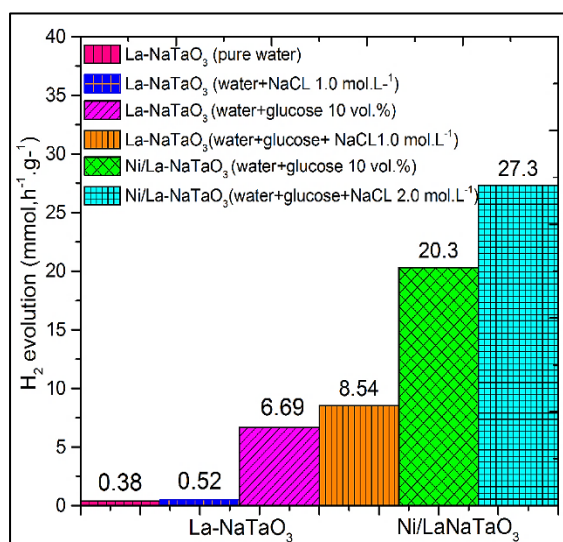
**Fig. 7:** Photocatalytic H<sub>2</sub> evolution over Ni/La-NaTaO<sub>3</sub> photocatalyst at various amounts of NaCl concentration, 0.3 wt.% of nickel and 10 vol.% glucose (0.1 mol.L<sup>-1</sup>)

The activity of Ni/La-NaTaO<sub>3</sub> with NaCl is much higher than that without NaCl. This phenomenon in the same trend was reported in previous literature (Li *et al.*, 2013), suggesting that with increasing NaCl concentration, the adsorption of glucose at Ni/La-NaTaO<sub>3</sub> increases, which can improve for glucose to combine photoinduce hole and hydroxyl radicals quickly. Therefore, with appropriate photocatalyst and electron donor, a high-efficient reaction system of saltwater could be constructed. The high photoactivity of Ni/La-NaTaO<sub>3</sub> may be attributed to the well-prepared nanocrystalline and good dispersion of nickel on the surface La-NaTaO<sub>3</sub>, as confirmed by SEM, TEM and XPS data.

As shown in **Figure 8**, the activity of the sample can be increased in the present of glucose as electron donor. In the absence of glucose, the photocatalytic hydrogen



generation is very low because of the recombination of photoinduced electrons and holes on semiconductor surface. The rate of hydrogen production has been found to be much higher, compared to that obtained from photocatalytic of pure water. This has been attributed to the effect of added glucose, which acts as sacrificial electron donor and consumes photogenerated holes and/or oxygen, thereby decreasing the rates of electron-hole recombination and H<sub>2</sub>-O<sub>2</sub> back reaction (Strataki *et al.*, 2010).



**Fig. 8:** H<sub>2</sub> evolution rate of La-NaTaO<sub>3</sub> and Ni/La-NaTaO<sub>3</sub> (350 ml of solution)

For comparison purposes with the results of other works, **Fig. 8** shows the highest values of H<sub>2</sub> evolution of the current work of 8.54 and 27.3 mmol.h<sup>-1</sup>.g<sup>-1</sup>, respectively, with the assistance of 0.3 g of La-NaTaO<sub>3</sub> and Ni/La-NaTaO<sub>3</sub> (0.3 wt.% Ni), 350 ml of aqueous solution. This result is about hundred times higher than Pt/Cd<sub>0.5</sub>Zn<sub>0.5</sub>S, reported by Li *et al.* (H<sub>2</sub> evolution 78 μmol g<sup>-1</sup> h<sup>-1</sup>, with the assistance of 0.2 g catalyst (1 wt.% Pt), 100 ml of aqueous solution 0.05 mol.L<sup>-1</sup> of

glucose, 0.10 mol/L NaOH (Li *et al.* 2011). The higher H<sub>2</sub> evolution of this work compared with Li *et al.*, was probably due to the La-NaTaO<sub>3</sub> compounds as a very efficient photocatalysts for hydrogen production (Kudo and Miseki, 2009; Husin *et al.*, 2017).

## CONCLUSIONS

The photocatalytic hydrogen production from NaCl solution over Ni/La-NaTaO<sub>3</sub> nanoparticles has been studied using glucose as a sacrificial reagent. The addition of an appropriate amount of NaCl to the reactant solution was shown to enhance H<sub>2</sub> evolution on Ni/La-NaTaO<sub>3</sub>, which is very important to practical application. Glucose can promote markedly photocatalytic hydrogen evolution. Glucose acting as an electron donor to scavenge photoinduced holes quickly so that the recombination of photoinduced electrons and holes at the Ni/La-NaTaO<sub>3</sub> surface and the back reaction of H<sub>2</sub> and O<sub>2</sub> are inhibited.

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