Research Article

Enhancing Hydrogen Production through Integration of Electrolysis and Photocatalysis in a Cell

Yohanes Engge, Frendi Maulana, Muhammad Nurhuda, Istiroyah and Lukman Hakim

1Physics Department, Faculty of Mathematics and Natural Sciences, Brawijaya University, Indonesia
2Weetebula Catholic University, Indonesia
3Department of Chemistry, Faculty of Mathematics and Natural Sciences, Brawijaya University, Indonesia

Correspondence should be addressed to Muhammad Nurhuda; mnurhuda@ub.ac.id

Received 14 June 2023; Revised 26 September 2023; Accepted 6 October 2023; Published 8 November 2023

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We present a new method for hydrogen production that combines photocatalysis and electrolysis in a cell. TiO₂ was doped with Ni and nitrogen to form Ni-TiO₂ and N-Ni-TiO₂ photocatalysts. XRD, UV-Vis, and SEM techniques were used to characterize the resulting samples. The Ni-TiO₂ and N-Ni-TiO₂ samples had anatase structures with energy gaps of 2.77 eV and 2.03 eV, respectively. A 50-watt UV lamp with a wavelength of 254 nm was used as the photon source. Our results indicate that this method produces more hydrogen than the sum of hydrogen generated by separate electrolysis and photocatalysis methods. The N-Ni-TiO₂ sample produced the highest yield of HHO gas among the Ni-TiO₂ and TiO₂ p.a samples. The underlying mechanisms responsible for this improvement, including the role of the Ni and nitrogen doping, are discussed and analyzed.

1. Introduction

Hydrogen is one of the most promising clean and sustainable energy carriers, producing only water as the final product, and thus ideal for electrochemical applications in fuel cells [1, 2]. On earth, hydrogen is generally found as component of other compounds, such as water (H₂O), methane gas (CH₄), hydrocarbons, amino acids, and carbohydrates [3].

Electrolysis process is a common method used to produce hydrogen from water by passing current to electrodes immersed in water. Compared to other methods, water electrolysis can produce hydrogen of high purity (99.99%), with the hydrogen produced being twice that of oxygen [4]. While the process can be sustainable and environmentally friendly when renewable energy sources such as solar or wind are used to provide the electrical energy resources, it is often considered inefficient as it requires a significant amount of electrical input power, which can make the process expensive. For example, a simple electrolysis of water with acidic or alkaline electrolytes yields 70% efficiency [5, 6].

Hydrogen generation via photocatalysis of water has also attracted the attention of many researchers [7]. Most photocatalysts are made from semiconducting materials because they have an energy gap that allows them to create electron-hole pairs when exposed to photons with a certain minimum energy. This formation of electron-hole pairs leads to the splitting of water molecules [8]. Fujishima and Honda reported the first experiments related to the splitting of hydrogen and oxygen using heterogeneous photocatalysts. Their approach uses a photoelectrochemical (PEC) cell that incorporates TiO₂ as the photoanode and platinum as the counter electrode, under exposure to UV light and an external potential [9]. Bard then applied this concept to design a photocatalysis system that uses semiconductor particles or powders as photocatalysts [10, 11]. Along with the development of it, several photocatalyst materials
have been identified and explored, such as $V_2O_5$ nanorods [12], CdS QDs/BiOI [13], and ZnO/CdTe [14]. To date, the field of photocatalyst technology has seen rapid progress and widespread use, including applications in water treatment and purification [15, 16].

$TiO_2$ is a semiconductor material that is widely used owing to its several advantages such as high stability, corrosion resistance, abundance in nature, relatively low cost, and nontoxicity [17]. However, the large energy gap of $TiO_2$ ($\sim 3.2$ eV) limits its use as a photocatalyst material for absorbing longer wavelengths of light. The reduced efficiency of $TiO_2$ in photocatalysis reactions arises not only from this energy gap but also from the rapid recombination of electrons and holes at the photocatalyst’s surface before interacting with water [18]. One way to reduce the energy gap of $TiO_2$ and the recombination of electrons and holes is by doping other materials to $TiO_2$, e.g., transition metal elements such as Mn, Cr, Ni, and Cu [19–22] and nonmetals, such as S, N, C, and P [23–26]. Several researchers have used doubly doped nonmetal ions and transition metals in $TiO_2$ (see, e.g., [27]) and successfully synthesized a Ni-N-$TiO_2$ photocatalyst that provides an energy gap of $2.4$ eV.

Based on the above considerations, it seems interesting to combine electrolysis and photocatalysis in a single cell (reactor) to increase the efficiency. This hypothesis is based on previous studies that a thin layer of $TiO_2$ on an electrode is an ideal photocatalytic agent for water electrolysis [28].

In this paper, we propose the use of photocatalyst materials in powder form, instead of as a thin layer on the anode or cathode, for two reasons. First, in powder form, the photocatalyst material has a much larger surface area, which increases its interaction with water and its ability to absorb photons. Second, we expect a synergistic interaction between photocatalysis and electrolysis. When the photocatalyst material absorbs photons, it produces electrons and holes. The electrolysis process facilitates the transport of these electrons and holes to the cathode and anode, respectively. This accelerates the water splitting process. To further accelerate water splitting, we dope the $TiO_2$ with N and/or Ni, which reduces the bandgap energy of the material. This allows the photocatalyst material to absorb a wider range of photons. Ni- and Ni-N-doped $TiO_2$ were synthesized using the sol-gel method to form a nanoparticle photocatalyst.

2. Methods

2.1. Photocatalyst Preparation and Characterization. Single-dopant $TiO_2$ (Ni-$TiO_2$) and double-dopant nitrogen and nickel (N-Ni-$TiO_2$) photocatalyst materials were prepared using the sol-gel method according to the following steps:

**Ni dopant synthesis:** first, 8.3 mL of 97% titanium isopropoxide (TTIP) from Aldrich was mixed with 143 mL of ethanol to obtain solution A. Solution B was prepared by adding 35 mL of ethanol and 3 mL of $HNO_3$ into 15 mL of demineralized water. Next, solutions A and B were mixed to form solution C, which was then stirred for 30 minutes at room temperature. Subsequently, 1% Ni (II) nitrate hexahydrate (precursor Ni) and 10 mL of demineralized water were added to solution C. The resulting mixture was stirred for 2 hours, left to stand for 24 hours, and then oven heated at 100°C for 15 hours. Finally, the product was calcined at 500°C for 2 hours, followed by crushing to obtain the powder form of Ni-$TiO_2$.

**N and Ni dopant synthesis:** initially, solution A was prepared by mixing 30 mL of ethanol, 1 mL of acetylacetone, and 8 mL of 97% TTIP from Aldrich. Solution B was then prepared by combining 2 mL of glacial acetic acid, 4 mL of demineralized water, and 30 mL of ethanol. Subsequently, solutions A and B were mixed and stirred for 30 minutes at room temperature. The doping process was initiated by adding 30 mL of demineralized water, 1.8 gram of urea (1 M), and 0.4003 g of Ni (II) nitrate hexahydrate to the mixture. The rest of the steps were the same as those for synthesizing Ni-doped $TiO_2$.

The synthesized photocatalyst materials were characterized using X-ray diffraction (XRD), UV-Vis spectroscopy, and SEM-EDS. XRD (Empyrean Cu LFF HR 9430 033 7310x) was used to determine the crystal structure, size, and phase of the photocatalyst materials. UV-Vis spectroscopy (SPECORD 200 PLUS-223E1117F) was used to measure the absorption spectrum of the samples and gather data on the wavelength and absorbance. The data were then analyzed using the Tauc plot method to obtain the band energy values. SEM-EDS was used to determine the morphology, particle size, and elemental composition of the samples.

2.2. Electrophotocatalysis Cell Design. Figure 1 shows the design of the reactor cell for the combined electrolysis and photocatalysis processes. The reactor consisted of an electrolyte solution container (1), electrodes made of SS 316 stainless steel (2) and (3), an electrolyte solution (4), a magnetic stirrer (5, 7), a UV lamp (6), an MQ-8 gas sensor (8), a container to capture bubble products (9), purified water (10), and a hydrogen-hydrogen oxygen (HHO) gas line (11, 12).

The process for producing hydrogen via simultaneous electrolysis and photocatalysis in a cell, hereinafter referred to as the “electrophotocatalysis,” was conducted as follows: first, the reactor is partially filled with 500 mL of demineralized water, and a quantity of the synthesized photocatalyst powder is dispersed in it. A small amount of methanol was then added as an electron-hole sacrificial agent, which acted as an electron donor or a hole scavenger to prevent recombination of electron holes and reverse reaction of $H_2$ and $O_2$ during the photocatalysis process [29, 30]. Additionally, natrium hydroxide (NaOH) was added to the solution to facilitate the electrolysis process. A 50 W/254 nm UVC lamp was used as the photon source for photocatalysis. To keep the photocatalyst suspended, the mixture was agitated during the observation process using a magnetic stirrer. The direct current (DC) supplying both electrodes was maintained at a constant level using Buck-Boost ZK-4KX. The hydrogen gas concentration was measured using MQ-8 gas sensor.

3. Results and Discussion

3.1. Photocatalyst Materials

3.1.1. Crystal Structure and Size. Figure 2 shows the X-ray diffraction results for the $TiO_2$ samples synthesized with
single Ni and double N-Ni dopants and TiO2 proanalysis (p.a) Merck for comparison. The pattern exhibits the characteristic diffraction peaks of TiO2 anatase structure at 2θ values of 25.30°, 37.80°, 48.05°, 53.91°, 55.08°, and 62.70° corresponding to crystal planes (101), (004), (200), (105), (211), and (204), respectively. The absence of any additional peaks in the N-Ni-TiO2 sample confirms that Ni and N were incorporated into the TiO2 lattice through substitution, replacing some O2- and Ti4+ lattice sites. This is because the ionic radii of N3- (1.46 Å) and Ni2+ (0.830 Å) are larger than those of O2- (1.40 Å) and Ti4+ (0.745 Å) [31].

In the case of the nickel-modified samples, in addition to the main anatase phase, there are minor amounts of rutile, brookite, and NiTiO3 phases. The rutile phase was observed at 2θ angles of 27.44° and 36.05°, which correspond to the (110) and (101) planes of rutile (JCPD card No. 21-1276) [32]. This is due to the Ni-induced phase transformation, whereby the Ni ions disrupt the crystal structure of TiO2 and promote the formation of rutile [33]. The brookite phase was observed at a 2θ angle of 30.83°, which corresponds to the (211) plane of brookite (JCPDS card No. 29-1360) [32]. The NiTiO3 phase was identified at 2θ angles of 33.04°, 41.25°, and 49.38° (ICDD File No. 04-006-6640), which is consistent with the previous reports [33–35].

The anatase phase is the most photocatalytically active crystalline form of TiO2 in Ni-TiO2 and N-Ni-TiO2 samples because it has a wider bandgap than rutile [36]. This allows anatase to absorb UV and visible light more readily, producing more electron-hole pairs for the photocatalysis reaction, which increases the efficiency of photocatalysis. Rutile is more thermally and mechanically stable than anatase, but it has a narrower bandgap and is therefore less photocatalytically active [37, 38].

The crystal size of each synthesized sample was determined using the Debye-Scherrer equation and FWHM analysis [39], as described by the following equation:

\[ D = \frac{K\lambda}{\beta \cos \theta} \]  

where \( D \) is the crystal size (nm), \( K \) is the crystal shape factor (0.9-1.0), \( \lambda \) is the X-ray wavelength (0.15406 nm), \( \beta \) is the FWHM value in radian, and \( \theta \) is the diffraction angle in degree. The results revealed that crystal sizes were 46.450 nm, 12.265 nm, and 7.120 nm for TiO2 p.a, Ni-TiO2, and N-Ni-TiO2, respectively. It suggests that doping TiO2 with N and Ni in general reduces the crystal size of the photocatalyst material.

The variation in crystal size of TiO2 samples doped with Ni and N-Ni had a significant impact on the photocatalysis water splitting process. Smaller crystals typically have larger surface areas and higher densities of active sites [40], which provide more surface area for water molecules to adsorb and facilitate efficient water splitting and hydrogen production. The smallest crystal size observed in the N-Ni-TiO2 sample suggests that this photocatalyst is highly efficient for hydrogen production.

The anatase crystal structure remains the dominant structure of the photocatalyst material, even when doped with Ni and N. This can be verified using the following two equations:

\[ 2d_{(hkl)} \sin \theta = n\lambda, \]  

\[ \frac{1}{d^2_{(hkl)}} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}, \]

where \( a, b, \) and \( c \) represent the lattice parameters, \( hkl \) is the index of the crystal planes, \( d_{hkl} \) stands for the distance between the crystal planes, \( \lambda \) is the wavelength of the incident X-rays (1.5406 Å), \( n \) is the diffraction order (chosen
as 1), and \( \theta \) denotes the diffraction angle in radians. For tetragonal crystal, the value of \( a = b \). Equation (2) was employed to extract the value of \( d \) from XRD peaks. Subsequently, by applying Eq. (3), we obtained the following lattice parameters: \( a = b = 0.37848 \) nm and \( c = 0.95124 \) nm for TiO\(_2\) p.a, \( a = b = 0.37852 \) nm and \( c = 0.94988 \) nm for Ni-TiO\(_2\), and \( a = b = 0.37858 \) nm and \( c = 0.95170 \) nm for N-Ni-TiO\(_2\). These results suggest that the incorporation of Ni and N dopants into TiO\(_2\) does not significantly alter the anatase crystal structures.

3.1.2. Optical Absorption of Photocatalyst Materials. The optical absorption spectra of TiO\(_2\) p.a and TiO\(_2\) doped with N and Ni were analyzed using UV-Vis spectroscopy. Figure 3 shows the absorption spectra of the synthesized photocatalysts at various radiation wavelengths. The UV-Vis absorption spectra show that the absorption peak of the TiO\(_2\) p.a sample occurs within the wavelength range of 350–400 nm, which is characteristic of anatase TiO\(_2\) [39]. In the visible light region (\( \lambda > 400 \) nm), the absorbance decreased and became flat. For the Ni-TiO\(_2\) sample, the absorption spectra shifted to the wavelength range of 350–550 nm, which corresponds to the UV and visible light spectral regions. The double-dopant N-Ni-TiO\(_2\) sample shows an even greater shift towards the wavelength of visible light, which is in the range of 400–600 nm. This is in line with the expectation that the presence of metallic and nonmetallic elements in TiO\(_2\) can improve its performance as a photocatalyst material in the visible light region.

The UV-Vis absorption spectra of the N-Ni-TiO\(_2\), Ni-TiO\(_2\), and TiO\(_2\) p.a samples correlate with the photon energy required to excite the valence band electrons to the conduction band. The bandgap energy of each sample was determined using the Tauc plotting method:

\[
(\alpha h\nu)^n = A(\nu - E_g),
\]

where \( \alpha \) is the absorbance coefficient, derived from the Lambert-Beer law:

\[
\alpha = 2.303 \times \text{absorbance values},
\]

where \( h \) is Planck’s constant, \( \nu \) is the frequency of light, \( E_g \) is the bandgap, and \( A \) is the proportional constant. The value of \( n \) is set to be 2 because the transition is direct, as it depends on the nature of the electronic transitions of the semiconductor [21].

The inset of Figure 3 shows curves representing the relation between \((\alpha h\nu)^n\) and photon energy \( h\nu \). To obtain the bandgap energy, we draw a straight line that represents the asymptotic slope of the curve. This line is extended until it intersects with the energy axis \( h\nu \). We found the bandgap energy values for each sample for TiO\(_2\) p.a, Ni-TiO\(_2\), and N-Ni-TiO\(_2\) to be 3.28 eV, 2.77 eV, and 2.03 eV, respectively. The N-Ni-TiO\(_2\) photocatalyst exhibited the lowest bandgap energy. This indicates that the double doping of metal (Ni) and nonmetal (N) is very effective in reducing the bandgap energy in TiO\(_2\) photocatalysts, owing to the synergistic effect of the two dopants. Thus, Ni dopants can generate new energy levels below the conduction band, while N dopants are above the valence band [33].

3.1.3. SEM-EDS Analysis. The analysis results using a scanning electron microscope (SEM) in Figure 4 show changes in the morphology and particle size of the TiO\(_2\) photocatalyst after being doped with N and Ni elements. In Figure 4 (b1) and (c1), it can be seen that there is little agglomeration in the sample, which consists of primary particles. Through SEM analysis and the use of ImageJ software, we were able to measure the distribution and average diameter of the primary particles in each sample. The measurement results show that the average particle diameter is 148.57 nm for TiO\(_2\) p.a, 31.67 nm for Ni-TiO\(_2\), and 21.00 nm for N-Ni-TiO\(_2\), as seen in Figure 4 (a2), (b2), and (c2). Both types of modified photocatalysts showed much smaller particle diameters compared to TiO\(_2\) p.a, and the difference in diameters was not significant between the doped samples.

Energy-dispersive X-ray spectroscopy (EDS) analysis was performed to confirm the successful doping of N and Ni elements in the TiO\(_2\) structure. In the single-doped sample (Ni-TiO\(_2\)) shown in Figure 5(b), three Ni peaks were detected at energies of 0.8 keV, 7.5 keV, and 8.3 keV. In the doubly doped sample (N-Ni-TiO\(_2\)) shown in Figure 5(c), the N peak was observed at 0.5 keV, while the Ni peak remained constant. These findings confirm the presence of N and Ni dopants in the TiO\(_2\) crystal structure, which could potentially alter the photocatalytic activity of the doped samples.

3.2. Electrophotocatalysis Experiment. Experiments on the electrolysis of water in combination with a photocatalysis process or electrophotocatalysis were performed in a reactor according to the procedure described in the preceding section. The photocatalyst materials used in this study were TiO\(_2\) p.a, Ni-TiO\(_2\), and N-Ni-TiO\(_2\).

The instantaneous concentration of hydrogen gas produced was measured as a function of time using an MQ-8 gas sensor. The total gas yield was calculated based on the number of bubbles released. The spitting rate of water is
proportional to the hydrogen concentration at any given moment because the HHO gas escapes the water tank without accumulating and maintains a constant pressure within the tank. Therefore, the total amount of hydrogen gas produced is proportional to the number of HHO bubbles generated during the experiment.

Figure 6 shows the experimental results of photocatalysis, electrolysis, and electrophotocatalysis for three different cases: (a) TiO$_2$ p.a (as control), (b) Ni-TiO$_2$, and (c) N-Ni-TiO$_2$ photocatalysts. In all cases, 1 gram of photocatalyst was suspended in an aqueous solution containing 500 mL of demineralized water, 5 mL of methanol, and 5 mL of 1 M NaOH solution. The current and voltage were set to fixed values of 0.5 A and 8.6 V, respectively. Each case was repeated thrice, and the results were averaged. During data collection, the voltage and current fluctuated by approximately 2.3%.

It can be seen from Figure 6 that the electrophotocatalysis process exhibits the highest instantaneous hydrogen density compared to the individual electrolysis and photocatalysis processes. It also shows that the hydrogen production activity noticeably increased during the first six minutes and then linearly progressed. This could be due to the fact that all components involved in the reaction process work at their peak performance during the initial stages and then decline as the reaction progresses (see, e.g., Cao and Piao [41]). We observed photocatalyst deposits on the surface of the electrodes, although the difference was not significant. Furthermore, agglomeration and sedimentation of the photocatalyst could also reduce hydrogen production in the water splitting process [42].

It can also be seen from Figure 6 that the highest instantaneous hydrogen density was due to the N-Ni-TiO$_2$...
photocatalyst, followed by Ni-TiO₂, and finally TiO₂ p.a. This is a strong evidence that the two dopants clearly play a synergistic role in enhancing the photocatalysis activity of TiO₂ compared with that of a single dopant [33]. The synergistic role of nitrogen and nickel dopant in N-Ni-TiO₂ sample is that nitrogen dopant reduces the energy bandgap of TiO₂, allowing it to absorb more light energy in a wider wavelength range. Correspondingly, the nickel dopant also contributes to energy bandgap reduction and acts as an electron trap, which helps reduce the recombination rate of electron-hole pairs during the water splitting reaction process. As a result, N-Ni-TiO₂ can produce more hydrogen gas from the water splitting process compared to the other two materials.

The role of photocatalysts and electrolytes in electro photocatalysis water splitting might be described as follows: photocatalysts absorb photons of light and generate electron-hole pairs. The electrons then participate in the reduction of water to produce hydrogen, while the holes participate in the oxidation of water to produce oxygen. Electrolytes facilitate the flow of electricity between the photocatalyst and the electrodes, promote electrochemical reactions, and maintain the stability of the solution throughout the process. The presence of a photocatalyst and an electrolyte creates an electrostatic equilibrium that drives the overall water splitting reaction. This equilibrium could be essential for achieving high efficiency in hydrogen production.

To measure the performance of the electrophotocatalysis process more accurately, we define “gain” as the difference between the instantaneous hydrogen density obtained from electrophotocatalysis and the sum of the instantaneous hydrogen density from photocatalysis and electrolysis. Figure 7 shows that the gain in instantaneous hydrogen density is highest for Ni-N-TiO₂ among the three samples.

Since the instantaneous hydrogen density only represents the proportion of the yield, so it is also important to consider the total yield of hydrogen. This was done by counting the number of generated HHO bubbles. Since HHO gas is a mixture of hydrogen and oxygen gases in a 2:1 ratio, so the portion of hydrogen in HHO gas is 66.67%. In the inset of Figure 7, we show the number of bubbles generated through the electrophotocatalysis process as blue bars, while the gains are displayed as yellow bars. The number of bubbles generated for TiO₂ p.a, Ni-TiO₂, and N-Ni-TiO₂ were 209, 220, and 250 bubbles, respectively, while the respective gains were 28, 35, and 61.

The origin of the enhancement of hydrogen yield in the electrophotocatalysis reaction might be as follows: it is known that water is a polar molecule, which is slightly positively charged on the hydrogen atoms and slightly negatively charged on the oxygen side. The electrons in the water molecule are more concentrated around the oxygen atom, resulting in a partial negative charge. In contrast, the hydrogen atoms have a partial positive charge as a result of electron displacement towards the oxygen atom. In the presence of a photocatalyst material, the formation of electron-hole pairs may increase the polarity of H₂O molecules. This phenomenon is consistent with the findings of Hribar et al., who reported that the structure of water is strongly affected by electrostatic equilibrium when ions are present around a water molecule [43]. Consequently, the presence of a photocatalyst would also affect the electrostatic equilibrium of water and hence reduces the dissociation energy of the water molecules. When an external electric field is applied through the electrode plates, the binding energy between hydrogen and oxygen in the polarized water affected by the photocatalyst is more easily broken than that without photocatalyst activation. This is confirmed by our experiments; in the
Figure 6: Comparison of the instantaneous hydrogen density obtained through electrolysis, photocatalysis, and electrophotocatalysis reaction with respect to different photocatalyst material.
3.3. Effect of Sacrificial Agent and Electrolyte on Electrophotocatalysis Water Dissociation. It is known that the concentration of ions strongly affects the charge transport in cells and determines the performance of water electrolysis. We performed a series of experiments to observe the variation in the NaOH catalyst and methanol as the sacrificial agent. Two different treatments were performed: the first consisted of varying the concentration of methanol and keeping the concentration of NaOH fixed, while the second consisted of varying the amount of NaOH catalyst without addition of methanol.

Figure 8 shows the results of the electrophotocatalysis experiment obtained by varying the amount of methanol. In this case, 1 gram of Ni-N-TiO₂ photocatalyst and 5 mL of NaOH solution with a concentration of 1 M were dissolved in 500 mL of demineralized water. Four different amounts of methanol were used, i.e., 0 mL, 5 mL, 10 mL, and 15 mL. The current supplied to the cell was set to 0.5 A, while the voltage was set 8.6 V.

We can see that adding methanol had a minimal impact on hydrogen yield. Initially, the instantaneous hydrogen density was lower without or with minimal methanol addition, but it reversed as the reaction progressed. The average instantaneous hydrogen density after completing the experiment was 215 ppm for 0 mL methanol addition and 226 ppm for 5 mL. However, adding more methanol decreased the instantaneous hydrogen density. This reverse trend is likely due to a decrease in the pH level of the solution. We observed that the pH levels were 12, 11, 10, and 9 for the 0 mL, 5 mL, 10 mL, and 15 mL of methanol addition to solutions, respectively.

Figure 9 shows the effect of NaOH concentration on the instantaneous hydrogen density without the addition of methanol. Other parameters were kept the same as in the previous experiments. The instantaneous hydrogen density production was minimal without NaOH, indicating that the photocatalyst alone contributes little to hydrogen production. As more NaOH is added, the instantaneous density of hydrogen production increases. This is likely due to the increase in OH⁻ ions, as a higher concentration of OH⁻ ions results in a higher conductivity, which facilitates the flow of electric current during electrolysis. The pH values of the solutions were 7.7, 11.9, and 13.2 for NaOH amounts of
0 mL, 5 mL, and 10 mL, respectively. Furthermore, doubling the amount of NaOH from 5 mL to 10 mL increased the instantaneous density of hydrogen production by 40%. For the results shown in Figure 8, the average instantaneous density of hydrogen was only 215 ppm when 5 mL of NaOH was added. By doubling the amount of NaOH used, a higher yield of 302 ppm was achieved.

It is well known that more alkaline in electrolysis can favor to the oxygen evolution reaction (OER), which is the rate-limiting step in the electrophotocatalysis process. This is because the OER is an electrochemical reaction that requires the presence of OH− ions [44]. Therefore, the concentration of NaOH is an important parameter to consider when optimizing the electrophotocatalysis process for hydrogen production.

4. Conclusion

In conclusion, we have demonstrated electrolysis combined with a photocatalytic process (electrophotocatalysis) in a cell for more efficient hydrogen production using different TiO2 catalysts doped with Ni and Ni-N. The samples of Ni- and Ni-N-doped TiO2 photocatalysts were synthesized using sol-gel method. XRD analysis shows that both materials are dominated by anatase structures in the nanomaterial dimension. From UV-Vis spectrum analysis, the energy bandgap values were found to be 2.77 eV and 2.03 eV for Ni-TiO2 and N-Ni-TiO2, respectively. We have found that the simultaneous combination of electrolysis and photocatalysis in the cell can increase hydrogen production compared to the sum of the electrolysis and photocatalysis yields in separate reaction. The gain ranged from 0 to approximately 21%, with the N-Ni-TiO2 photocatalyst providing the highest yield owing to its larger optical absorption at longer wavelengths and its relatively smaller energy bandgap. Furthermore, only a small effect of the sacrificial addition (methanol) on the hydrogen yield was observed, whereas the concentration of the electrolyte catalyst turned out to be a much more dominant factor.

Data Availability

All data is now in figure files. Double-clicking a figure file will open it in its original format in Origin.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

This work was supported by a special research grant program for doctor and professors of the Faculty of Mathematics and Natural Sciences, Universitas Brawijaya, under the contract number 20/UN10.F09/PN/2020. YE and FM gratefully acknowledge the YAPNUSDA/STKIP Weetebula-MISEREOR/KZE Cooperative Program for the financial support during the course of the work.

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