Enhanced Photoelectrocatalytic Performance of TiO_2 Nanorods in Photoelectrochemical Water Splitting Cell by Using an Alcoholic Sacrificial Agent

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Abstract

Photoelectrocatalytic water splitting by using various TiO_2 nanostructures is a promising approach to generate hydrogen without harmful byproducts. However, their effective performance is restricted by some drawbacks such as high rapid electron-hole pair recombination and backward reaction producing H_2O. Thus in this study, the probability of enhancing hydrogen generation rate by adding methanol as a sacrificial agent to the anodic chamber of a two-compartment photoelectrochemical cell is investigated. Herein, one-dimensional elongated TiO_2 nanorods that were fabricated via a facile one-pot hydrothermal method are utilized as potent photoanode. Voltammetric characterizations confirm that addition of alcoholic sacrificial agent has a significant effect on photoelectrochemical properties of TiO_2 nanorods which by adding 10 wt% of methanol, the photocurrent density and photoconversion efficiency increased from 0.8mA.cm^{-2} to 1.5mA.cm^{-2} and from 0.28% to 0.45%, respectively. The results of photoelectrocatalytic water splitting indicated that the hydrogen generation rate in the presence of methanol was about 1.2 times higher than that from pure water splitting. These enhancements can be attributed to the key role of methanol. Methanol molecules not only inhibit the electron-hole pair recombination but also accelerate the hydrogen generation rate by sharing their hydrogen atoms.

Key words: TiO_2 nanorods, Water splitting, Photoelectrocatalyst, Sacrificial agent, one-pot hydrothermal

1. Introduction

Nowadays, the rapid population growth and economic development of industrialized countries have increased the demand for energy. Currently, most of the world's energy acquires from fossil fuels reserves. However, fossil fuels are not renewable and their reserves are depleted progressively. Furthermore, the combustion of fossil fuels emits greenhouse gases that largely participate in the global warming problem. Accordingly, finding an alternative energy source is very obligatory [1].

In today's societies, hydrogen is considered as a promising clean energy carrier that has high energy content per weight and is environmentally benign [2]. The major obstruction towards using hydrogen energy instead of fusil fuels is that most of the technologies currently used to produce hydrogen consume fossil fuels to achieve their energy requirements [3]. In this regard, around 50% of the global hydrogen is met by natural gas steam reforming, 30% from oil reforming, 18% from coal gasification and 4% from other sources [3,4]. To solve this problem, many efforts have been invested to find a proper way for the production of hydrogen. As a consequence, photoelectrocatalytic hydrogen generation via water splitting, which can convert solar energy into storable chemical fuels, has been broadly recognized as a favorable example of artificial photosynthesis [6,7].

In a conventional photoelectrocatalytic process, the water is oxidized at the photoanode to generate oxygen while hydrogen is produced at the cathode by reduction of water or generated protons from photoanode [8]. In this process, the reduction reactions are depended to the transportation of photo-generated electrons through an external circuit from the photoanode to the cathode [9]. Thus, choosing a suitable photocatalyst to use as a photoanode is a key factor in photoelectrocatalytic water splitting. It is worth noting that the water reduction reaction occurs at 0 V vs. NHE (H^+/H_2) while the water oxidation reaction happens at 1.23 V vs. NHE (H_2O/O_2) [10]. Therefore, the conduction band of photocatalyst needs to be at a potential less than 0 V while the valence band needs to be at a potential more than 1.23 V. To date, a wide range of semiconductors such as TiO_2, ZnO, Fe_2O_3, $BiVO_4$, WO_3, CdS, and GaN have been applied for the hydrogen production in photoelectrocatalytic systems [11]. Among the different semiconductors, TiO_2 is known as a good candidate for photoelectrocatalytic hydrogen production due to its unique characteristics such as appropriate energy band position, superhydrophilicity, non-toxicity, high chemical stability and low cost [12,13]. According to the published reports in recent years, between the various TiO_2 nanostructures, one-dimensional elongated TiO_2 nanorods can significantly grant the unidirectional percolation paths for photo-excited charge carriers by providing better connectivity, thus possessing high photoelectrocatalytic activity in hydrogen production [7,14].

However, the impressive photoelectrocatalytic hydrogen production suffers from two drawbacks including rapid recombination of electron-hole pairs as well as a large driving force for the backward reaction producing H_2O [15]. To address these issues, various strategies have been employed to improve the photoelectrocatalytic efficiency of TiO_2 nanorods. Recent research demonstrates that the addition of electron donor molecules or in the other words sacrificial reagents is an effective approach to enhance the hydrogen generation rate in photoelectrocatalytic systems [16]. Sacrificial agents by capturing the active spices, i.e., photo-generated holes, inhibit the electron-hole pair recombination as well as prevent backward reaction producing H_2O [17]. In addition, sacrificial agents by contributing their hydrogen atoms can increase hydrogen generation rate [18].

According to the best of our knowledge, the effect of the sacrificial agent on the photoelectrochemical properties of TiO_2 nanorods for using in water splitting system has not been investigated so far. Hence, the aim of this study is to evaluate the contribution of the sacrificial agent on the overall rate of photoelectrocatalytic hydrogen evolution from water splitting. For this purpose, TiO_2 nanorods are fabricated by the facile one-pot hydrothermal method and the effect of using methanol as an alcoholic sacrificial agent are investigated on photoelectrochemical properties and photoelectrocatalytic activity of TiO_2 nanorods in hydrogen generation.

2. Experimental

2-1- Materials

All chemicals in the analytical reagent grade were used as received without further purification, and all solutions throughout experiments were prepared with deionized water. Methanol, ethanol, acetone, picric acid (PA), sodium sulfate (Na_2SO_4), tetra butyl titanate (TBT), hydrochloric acid (HCl), titanium tetrachloride ($Ticl_4$), hydrofluoric acid (HF) and nitric acid (HNO_3) were all Merck chemicals. Commercial titanium sheet with a thickness of 0.5 mm and a purity of 99 % was used for fabricating the TiO_2 nanorods. Before using the Ti sheet, it was polished chemically in a mixture of HF, HNO_3 and distillated water solutions with a volume ratio of 1:4:5.

2-2- Preparation of TNRs

The polished Ti sheets were pretreated by soaking them in a $TiCl_4$ aqueous solution at 70 ˚C for 50 min. Then, the treated Ti sheets were washed with deionized water, and then annealed at 450 ˚C for 1h. Subsequently, the hydrothermal procedure was utilized to fabricate TiO_2 nanorods (TNRs) as follows: 30 ml H_2O and 30 ml HCl (36.5–38 wt.%) were mixed with 6 ml methanol to reach a total volume of 66 ml. Then, 0.23g PA was added into the above solution under stirring for 10 min at ambient conditions. Afterward, 0.5 mL TBT was subjoined under vigorous stirring until dissolved completely. Then, the mixture was transferred to a Teflon-lined stainless steel autoclave and one piece of pretreated Ti sheet was placed at an angle in the Teflon with the seeding layer facing down. The hydrothermal reaction was conducted at 160 ˚C for 12 h. Finally, the as-fabricated TiO_2 nanorods on Ti substrate were rinsed with distilled water and annealed in air at 450 ◦ C for 2 h with a heating rate of 3 ˚C/min.

2-3- Characterization

The surface morphology, length, and diameter of the as-synthesized samples were determined by a field-emission scanning electron microscopy (FESEM; Hitachi S4160, Japan) and the elemental composition was estimated by energy dispersive X-ray spectroscopy (EDX).

2-4- Photoelectrochemical evaluation

The photoelectrochemical performance was measured using potentiostat/galvanostat (PGS-8, Sharif Solar, Iran) in 0.1M Na_2SO_4 electrolyte with a standard three-electrode cell consisted of the achieved TiO_2 nanorods, platinum foil, and Ag/AgCl as the working, counter and reference electrodes, respectively. The working electrode (active area: 8 cm^2) was illuminated by a UV light source (315–400 nm) with the light intensity of 100 $mWcm^{-2}$. All the photoelectrochemical measurements were performed for general presentation under air condition.

2-5- Hydrogen production performance

The evolution of hydrogen was performed through the water splitting in a two-compartment photoelectrochemical cell (PEC). As illustrated in Fig. 1, the PEC cell was separated into an anodic chamber and a cathodic chamber by a Nafion membrane, which each chamber was filled with 0.1 M Na_2SO_4 electrolytes. The synthesized TNRs, Ag/AgCl and Ti sheet served as the photoanode, reference electrode, and cathode, respectively. The hydrogen was generated on the cathodic chamber by applying 1 V bias voltage vs. Ag/AgCl under UV irradiation. An inverted burette with displacing electrolyte in the burette column was employed to collect hydrogen gas generated at the Ti electrode. The volume of H_2 was directly determined by reading the variation of electrolyte level. Moreover, to investigate the effect of the sacrificial agent, the above procedure was executed in the presence of 10 wt.% methanol in the anodic chamber.

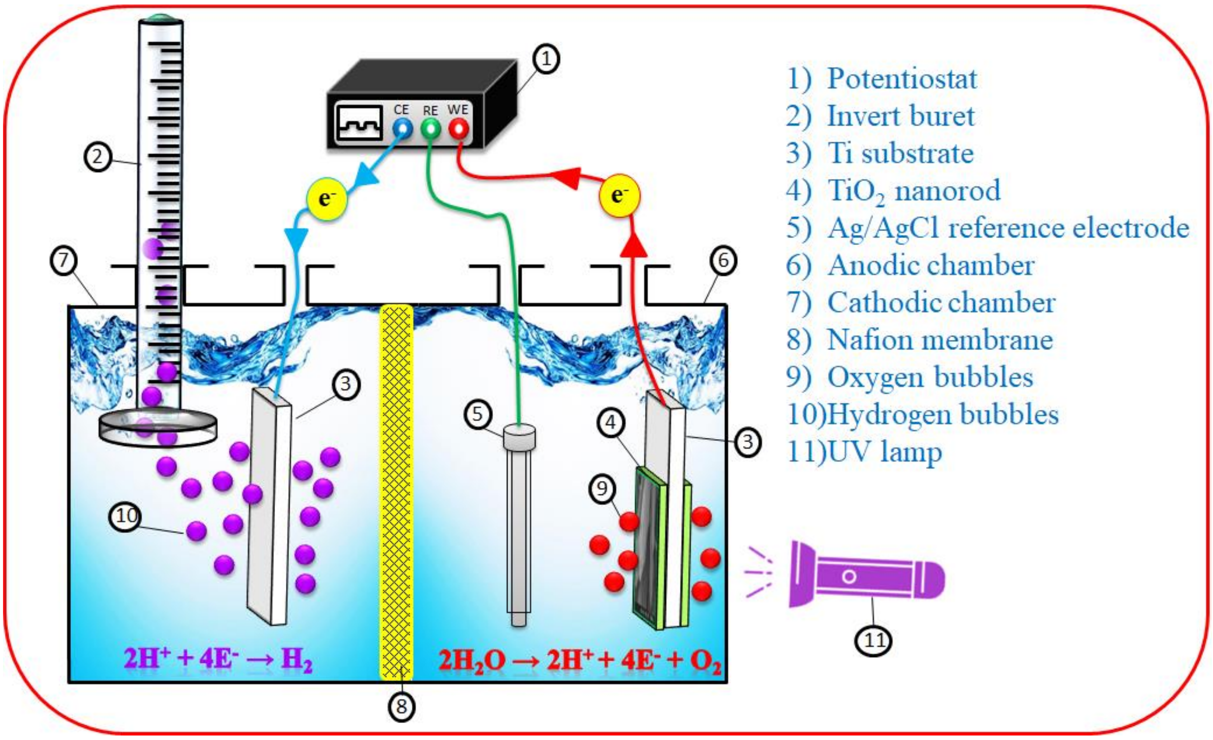

Fig. 1. Schematic illustration of the photoelectrocatalytic water splitting

3. Results and discussion

3-1- FESEM

To investigate the morphology and the elemental composition of the as-prepared TNRs, the FESEM and EDX analysis were performed and the results are presented in Fig. 2. According to the cross-sectional FESEM that are shown in Fig. 2(A), it can be observed that the hydrothermal procedure led to the successful formation of vertically-aligned, smooth and dense nanorods with an average length of about 300 nm on the Ti substrate. The top view of the TNRs is exhibited in Fig. 2(B). Based on this image, it can be seen TNRs have the quadrangle-shaped surface with an average side length of about 250 nm.

Fig. 2(C) presents the EDS spectra of the as-prepared photocatalyst. The EDS analysis of TNRs shows a peak around 0.4-0.5 keV, and another intense peak appears at 4.5 and 4.9 keV for Ti. Based on Fig. 2(C), the TNRs completely consisted of Ti and O atoms with a mass percentage of 66.15% and 33.85%, respectively.

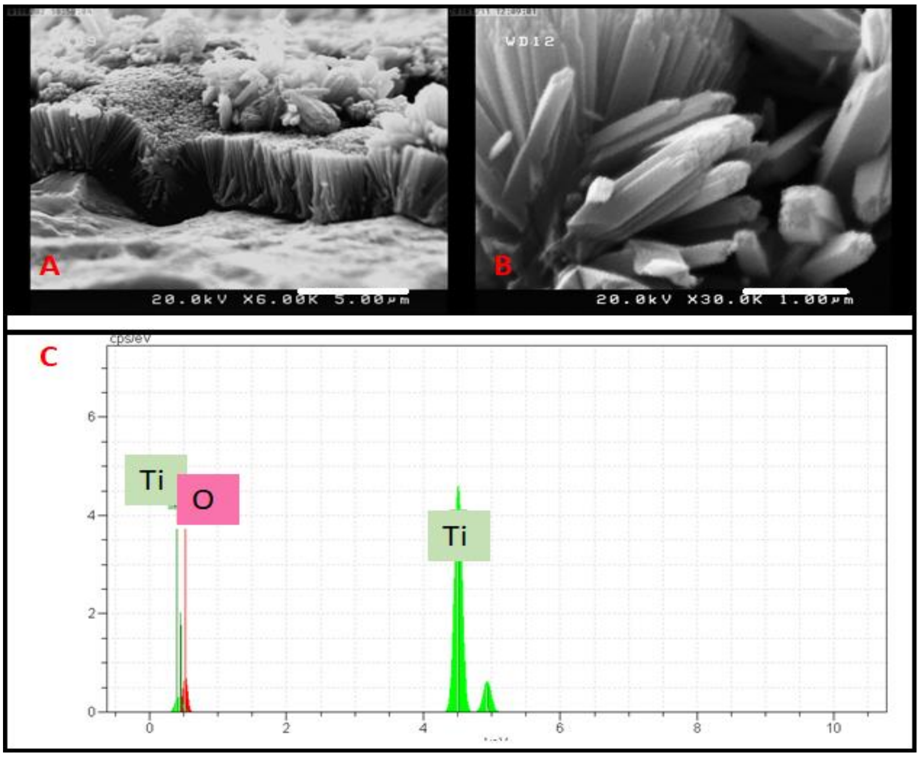

Fig. 2. FESEM images of (A) cross section of TiO_2 nanorods, (B) top surface of TiO_2 nanorods, and (C) EDX analysis of TiO_2 nanorods.

3-2- Photoelectrochemical measurement

Photocurrent measurement was used to evaluate the charge separation in the as-prepared photocatalysts. In this regard, larger photocurrent means higher separation efficiency and more photo-generated electrons. The characteristics of the photocurrent density-voltage (j-V) curves were recorded under UV illumination, and are demonstrated in Fig. 3.

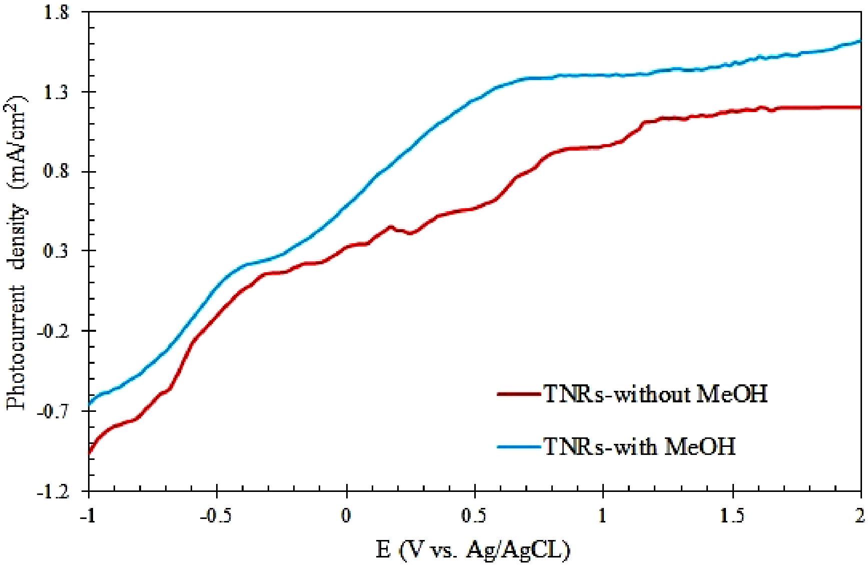

Fig. 3. Linear-sweep voltammograms measured from TiO_2 nanorods in the presence and absence of methanol

As shown in Fig. 3, methanol has a significant effect on photocurrent density. The photocurrent density in the presence of methanol was 1.5mA.cm^{-2} at 1V vs. Ag/AgCl that it was 1.87 times more than the photocurrent density in the absence of methanol in anodic chamber. This result indicates that the photo-generated electrons on the nanorods in the presence of methanol can be faster transported to the counter electrode, and greater water splitting efficiency can be expected.

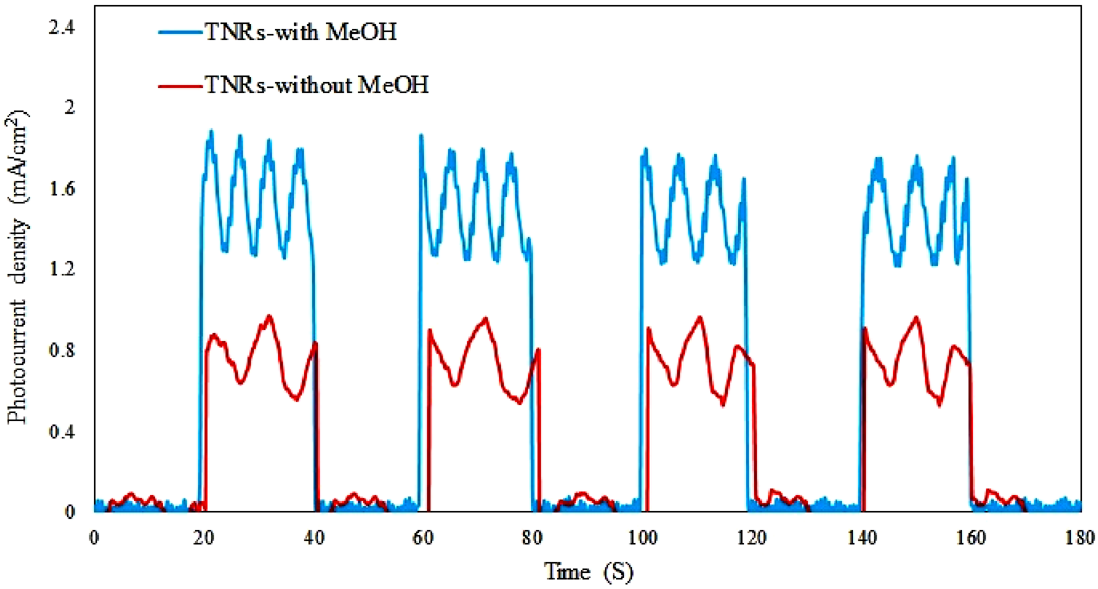

Fig. 4. The transient photocurrent response curves of TiO_2 nanorods in the presence and absence of methanol at 1V vs. Ag/AgCl in 0.1M Na_2SO_4 under UV

Fig. 4 shows the transient photocurrent density of TNRs photoanode by several on-off cycles under the UV illumination. It should be attended that the photocurrent went down to zero as soon as the irradiation of light was stopped, while subsequently shifted to original value as soon as the light was switched on again, implying that the photo-generated current was completely effectuated by the activity of the as-fabricated TNRs photoanode.

The hydrogen production efficiency (photoconversion efficiency) of the prepared samples is determined by the following equation [17]:

$$\eta\ (\%) = j_p \left[\frac{E^o_{rev} - |E_{app}|}{I_o} \right] * 100$$

where η is the photoconversion efficiency, j_p is the photocurrent density (mA.cm^{-2}), I_0 means the intensity of the incident light, E^0_{rev} represents the standard changeable potential (1.23 V vs. RHE), and $|E_{app}|$ denotes the absolute value of the applied voltage which is obtained from $E_{app}= E_{meas}- E_{aoc}$, where E_{meas} is the electrode potential (vs. Ag/AgCl) at which j_p is measured and E_{aoc} is the electrode potential (vs. Ag/AgCl) at open circuit under illumination. Plots of photoconversion efficiency with applied potential are presented in Fig. 5.

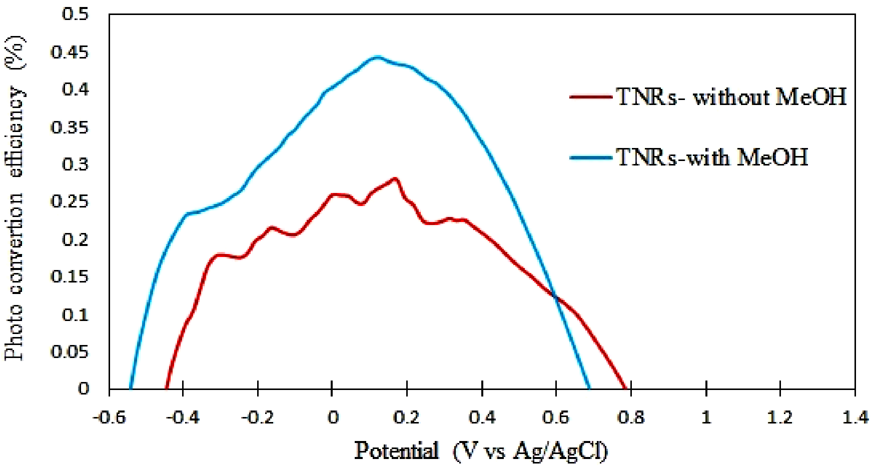

Fig. 5. Photoconversion efficiency of TiO_2 nanorods in the presence and absence of methanol

Based on Fig. 5, it can be observed that using methanol as sacrificial agents dramatically intensifies the photoconversion efficiency. A maximum photoconversion efficiency of 0.45% is obtained in the presence of methanol, while it is only 0.28% in the absence of methanol at 0.2 V (vs. Ag/AgCl). To sum up, the improvement of photoconversion efficiency and photocurrent density of TiO_2 nanorods is attributed to the scavenging role of MeOH. In other words, MeOH can prevent the recombination of electron-hole pairs by capturing the photo-generated holes. Therefore, more electrons can be transferred from photoanode to cathode and greater water splitting can be expected.

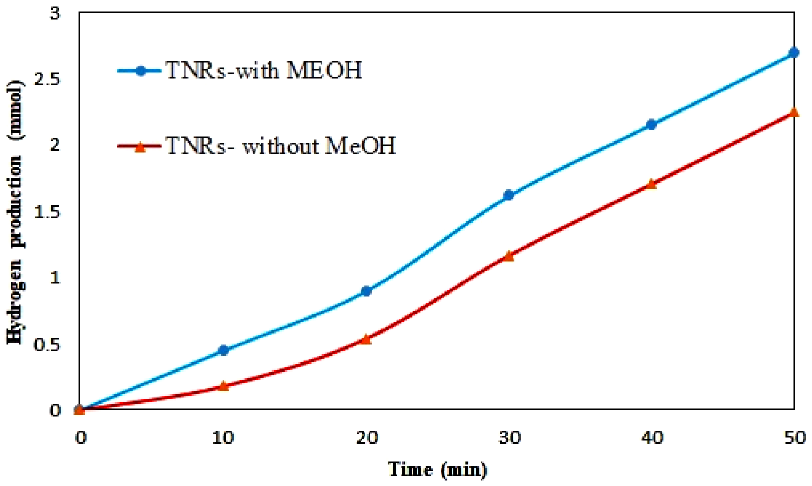

Fig. 6. Effect of the methanol on the photoelectrocatalytic activity of TiO_2 nanorods in hydrogen generation

3-3- Photoelectrocatalytic performance

Fig. 6 presents the amount of generated hydrogen in both the presence and absence of methanol in the anodic chamber. According to the results, the amount of generated hydrogen in the presence of methanol was 2.75 mmol which was 1.2 times more than the amount of generated hydrogen in the absence of methanol. Furthermore, the rate of hydrogen production (mmol.min^{-1}) was calculated with respect to the slopes obtained from the hydrogen mole–time curves (Fig. 6) and the result is exhibited in Fig.7. As shown in Fig. 7, it can be observed that the presence of methanol as sacrificial agents in the anodic chamber can increase the hydrogen production rate from 0.047mmol.min^{-1} to 0.055mmol.min^{-1}.

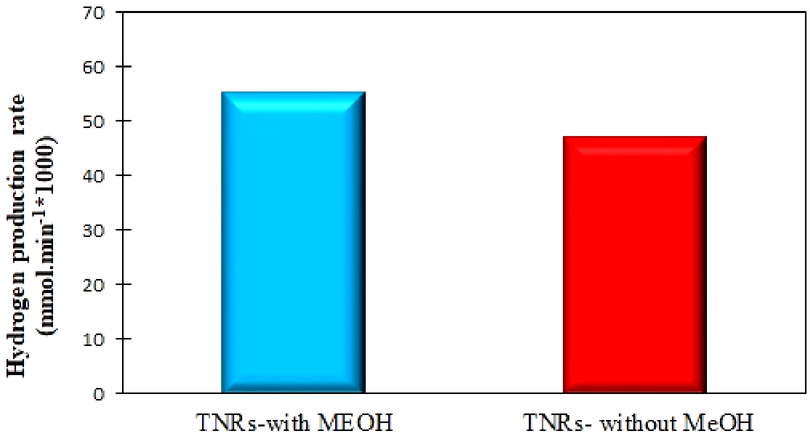

Fig. 7. Effect of the methanol on the rate of photoelectrocatalytic hydrogen generation

These data prove the significant role of methanol as a sacrificial agent in hydrogen generation. Methanol enhances the rate of separating electron-hole pairs and decreases the amount of electron-hole recombination. Therefore, as a consequence of the improvement of photocurrent density and photoconversion efficiency, the hydrogen generation rate boosted in presence of Methanol in the anodic chamber.

4. Conclusion

In a summary, this work has demonstrated the photoelectrocatalytic activity of TiO_2 nanorod in the presence of methanol for the hydrogen generation from the water splitting. The result showed that the one-pot hydrothermal method is an appropriate procedure to fabricate one-dimensional elongated TiO_2 nanorods on a titanium substrate. The photoelectrochemical investigation revealed that the photocurrent density and photoconversion efficiency in the presence of methanol are 1.87 and 1.2 times more than their value in the pure Na_2SO_4 electrolyte. As a consequence of the improvement in photoelectrochemical properties, the addition of methanol led to the improvement of the hydrogen production rate from $0.047 mmol.min^{-1}$ to $0.055 mmol.min^{-1}$. Therefore, this work could propose a new opportunity to utilize photoelectrocatalytic water splitting as a low-cost and efficient manner for producing clean energy in the future.

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