Hydrogen Production from Photocatalytic Water splitting in Optofluidic Microreactors

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Abstract
Due to the decrease in fossil fuel reserves worldwide and the need to find alternative and renewable fuels, Hydrogen is one of the best choices for replacing fossil fuels. But current methods and technology are not the answer. One of the promising methods for producing hydrogen is the use of optofluidic microreactors. The safest and best way to produce hydrogen is to use a water-splitting reaction. Water and sunlight are two indispensable sources of hydrogen. In this study, hydrogen production in an optofluidic microreactor using water and UV-irradiation was investigated. To study the feasibility of microreactors effect of different flow rate and iodide concentration has been tested.

Keywords: hydrogen production, microreactor, water-splitting

Introduction
Today, with increasing concerns about fossil fuel reduction and environmental problems, various research has been conducted on the development and use of alternative energy. According to BP forecasts, global energy demand will increase by 1.3% per year by 2035. [1] Suppose there is a 30% increase in toe power consumption if no change is made in the power generation sector.
The results indicate instability in the process of energy production systems or dependence on limited hydrocarbon resources (oil, gas, and coal). This can lead to increased greenhouse gas emissions and climate change and poses a serious threat to the environment. Given this, the need for a clean and sustainable energy source is essential. Among the alternative and new sources of energy, in particular, hydrogen can be considered as a reliable and promising energy factor due to its high efficiency, abundance and environmental sustainability. [2,3]
Among the renewable energy sources, solar irradiation is the most plentiful source of energy. It is evaluated that about 0.01% of the energy of one second of sunlight irradiation is enough for the annual energy usage of worldwide. However, one major challenge is using this type of energy and storing it for future applications. One promising way is to use hydrogen as an energy carrier to accumulate solar energy in the form of a chemical bond between two hydrogen atoms. This hydrogen molecule can then react with oxygen in the air to release its energy and produce water as a by-product that is completely environmentally friendly. [4,5]

The most challenging task in photocatalytic water-splitting is producing proper photocatalytic than can absorb UV-irradiation for water-splitting. In general, photolysis has three stages: excitation, mass propagation and surface transfer from charge carrier excitation. Therefore, an efficient photocatalyst should have some basic and important requirements according to the semiconductor and its chemical properties such as crystal structure and surface properties. Although many different semiconductors have been developed over the past decades, most of them need proper redox mediators to be activated and produce hydrogen under UV-irradiation. [6]

Photocatalytic water-splitting using TiO_2 for hydrogen production is a new way for hydrogen production using UV-irradiation. Also, Due to proper energy band structure and high photochemical stability of TiO_2, nanocrystalline TiO_2 photocatalytic water-splitting has great potential for low cost and environmentally friendly hydrogen production. Table 1 summarizes some advantages and disadvantages of TiO_2 as a photocatalyst for water-splitting hydrogen production. [7]

Table 1) Advantages and Disadvantages of TiO_2 as a photocatalyst in water-splitting process.

Advantages	*Disadvantages*
High photochemical stability	*Rapid recombination produced electron / hole pairs as well as back reactions*
Environmentally friendly solar hydrogen production	*The wide band gap of TiO_2 limits its use in the visible light region*
High resistance to corrosion	*High Potential for Hydrogen Generation on surface of TiO_2 Inactivates TiO_2 for Hydrogen Production*
Non-toxic	
It is abundant and cheap	
Easily produced in nanocrystalline form by simple "soft" methods such as the SOL-GEL process	

Despite the remarkable progress in photocatalysts, current water-splitting technologies have little efficiency. One reason is the poor performance of current hydrogen production reactors. Design and manufacture of reactors are key factors in the rate of water-splitting reaction. To counteract these limiting factors, high performance photoreactors must be designed that are qualified not only absorbing light effectively but also simplifying mass transfer. This goal is achieved by using the optofluidic method, which represents a new way of designing a photoreactor. [8,9]

The optofluidic is an emerging field to combine and exploit the benefits of optics and microfluidics. Such a combination has incomparable aspects such as appropriate flow control, large surface to volume ratio and short optical path. According to these features, the photon and high mass transfer at the micro-scale makes the optofluidic convenient for photocatalytic reactions. [10,11]

Water-splitting reaction

To describe water-splitting reaction over Pt/TiO_2 photocatalyst we use iodide/iodate as redox mediators. In this scheme, hydrogen and oxygen will be produced over photocatalyst and iodide and iodate mediators will work as redox factors. Water-splitting reactions are as follows:

$$IO_3^- + 6e^- + 3H_2O \rightarrow I^- + 6OH^- \quad (1)$$

$$4OH^- + 4h^+ \rightarrow 2H_2O + O_2 \quad (2)$$

$$I^- + 6h^+ + 6OH^- \rightarrow IO_3^- + 3H_2O \quad (3)$$

$$2H^+ + 2e^- \rightarrow H_2 \quad (4)$$

Oxygen production reaction over Pt/TiO_2 photocatalyst will occur whit high iodate concentration as shown in reactions (1) and (2), while hydrogen production reaction over Pt/TiO_2 photocatalyst will occur when high iodide concentration is used as shown in reactions (3) and (4). As a result, the rate of iodate/iodide depletion is related to hydrogen and oxygen production. Therefore, hydrogen production rate can be shown by injecting iodide solution into microreactors and monitoring iodide depletion efficiency, while oxygen production rate can be shown by injection iodate solution into microreactor and monitoring iodate depletion efficiency. [12]

Optofluidic Microreactor Device

Optofluidic microreactors with rectangular columns in length were fabricated using PMMA polymer and machining. The rectangular micro-grooved in the reaction chamber has a length, width, and height of 40*0.7 * 0.7 mm, respectively. The length, width, and height of the reaction chamber is 1 x 20 x 42 mm, respectively. Figure 1 shows an image of the microreactor made in this study.

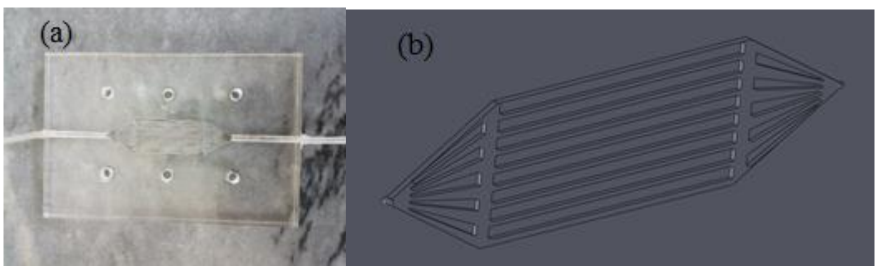

Figure 1) a) Image, b) schematic of optofluidic microreactor with rectangular micro-grooved

Fabrication of Pt/TiO_2 nanocatalyst

The appropriate amount of H_2PtCl_6 added to the water/titania nanofluid prepared under magnetic stirring. After 1 hour and production of milky solution, the appropriate amount of 0.1 M $NaBH_4$ solution is added to the solution and stirred again by magnetic stirring for 1 hour. By adding $NaBH_4$ solution and stirring for 2 hours by a magnetic stirrer, the color of the solution turns dark. The black sediments were then collected by centrifugation. After the sediment was washed with distilled water, the sediment was collected by filter paper. The precipitates collected were dried in oven for 12 h at 80 ° C and produced as a 1% w/w Pt/TiO_2 catalyst. [13] To produce the colloidal solution 1% w/w Pt/TiO_2 catalyst dissolved in 30 ml distilled water by a magnetic stirrer, then 0.2 ml of acetylacetone added to the solution and stirred for 1 hour. Then add 0.1 ml of Triton X 100 and stir again for 1 hour. [14]

Setup experiment

A 160-watt mercury vapor lamp was used to provide ultraviolet radiation. The feed is injected into the microreactor by a syringe pump. The solution was maintained by the addition of NaOH in Ph 12 to prevent the production of triiodide species and to make sure that the iodine species could correspond to oxygen and hydrogen production. Iodide and iodate have different peaks in UV, making spectrophotometry possible for any particular reaction. Therefore, the concentration of iodide in the reaction was measured by a UV spectrometer at 225 nm.

The effect of flow rate change on hydrogen production rate

In microreactor systems, the flow rate is one of the most important factors affecting microreactor performance. To investigate the effect of flow rate, the solution was pumped into the microreactor by a fusion 100 syringe pump at 50, 100 and 200 µl / min. An 80 µM iodide solution was injected into the microreactor to produce the same three discharges as hydrogen. As shown in Figure 2, iodide depletion efficiency decreased with increasing inlet discharge.

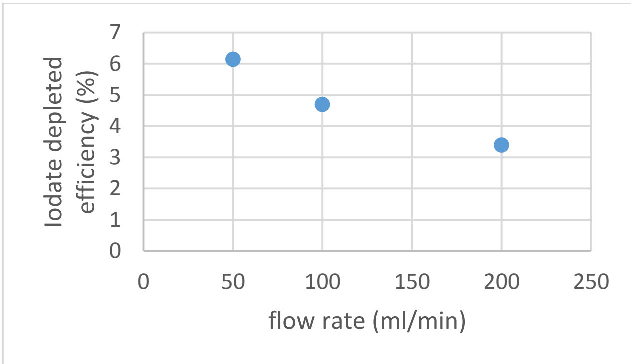

Figure 2) Effect of the flow rate on photocatalytic output for hydrogen-producing reaction

Because of the higher residence time of reactants in the reaction chamber of microreactor in lower flow rates, reactants have more efficient contact with Pt/TiO_2 photocatalyst which results in relatively higher iodide depletion in lower flow rates. Also, low current discharge reduces the amount of input load to the system, which also helps to reduce the iodine further. It can be found that iodide depletion efficiency decreases with increasing flow rate. The reason is that mass transfer in lower flow rate is more advanced that makes the efficiency far greater.

Effect of iodide concentration on hydrogen production

In the previous section, the concentration of the iodide solution was equal to 80 µM. To investigate the effect of iodide concentration on the production rate, concentrations of 80, 160 and 240 µM iodide were prepared and used. The inlet flow rate of microreactor in this experiment was set to 100 µL / min. As shown in Figure 3, iodide depletion efficiency decreased with increasing iodide concentration.

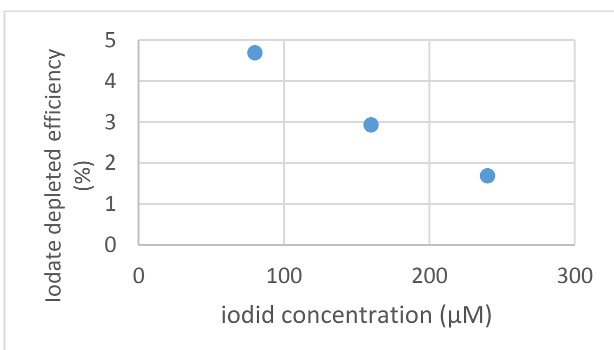

Figure 3) Effect of the iodide concentration on photocatalytic output for hydrogen-producing reaction

This decrease can be attributed to the following two aspects. First, an increase in iodide concentration has led to an increase in the load on the micro-grooved reactor. The capability of microreactors is limited such that high iodide concentration reduces the efficiency of iodide depletion. Second, although higher iodide concentrations can enhance mass transfer, more intermediates on the active surfaces of the catalysts are created and adsorbed simultaneously. As such, the large active surfaces covered by high iodide concentrations inhibit the reaction between the reactants and, as a result, the reaction rate decreases.

Conclusion

In this research, an optofluidic microreactor with a photocatalyst that loaded on the surface of a rectangular micro-grooved was fabricated. The possibility of this method and design was tested by a UV-irradiated photocatalytic test. The results showed that hydrogen can be produced using this method and the effect of flow rate and iodide concentration were investigated. Experimental results also revealed that the amount of hydrogen produced increases with decreasing the flow rate and lower iodide concentration.

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