

DEVELOPMENT OF LIGHT-DRIVEN H₂/O₂ GENERATION CHIP FOR MICRO FUEL CELL DEVICES

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ABSTRACT

At present work, we report on the development of fuel generation chip driven by the solar light for portable micro fuel cell devices. In the chip, fuel (H₂ and O₂) are generated by the integrated photocatalytic water splitting system utilizing bottom up and top down technologies. Generated gases are separated by specially designed hydrophobic modified channels. We describe the device concept and fabrication technologies to integrate the photocatalytic system (which is based on TiO₂ brush type nanorods structure) in the microchip. Also we demonstrate the working principle of the H₂/O₂ generation microchip under the solar light and the maximum of photocurrent density ~35-20 μA/cm² has been recorded during the gas generation and separation.

KEYWORDS

Fuel generation, Light-driven, Photocatalytic water splitting, Gas-liquid separation.

INTRODUCTION

Recently micro fuel cells have been considered as a new potential power source such as powerful batteries for portable devices. Traditional fuel cells require an external fuel supply system which leads difficulties for device miniaturization. To develop a new type of micro fuel cell, we have to combine micro fuel cells with the micro fuel generation device. The photocatalytic water splitting is suitable for the internal micro fuel generation device. Then, the combined device can be driven “just by solar energy”, where separation of the generated H⁺ and H₂, O₂ is required. Conventionally, such separation was achieved by utilizing proton exchange membrane (PEM). However, PEM has difficulty in micro integration due to low mechanical strength and deterioration in short time [1]. On the other hand, we already reported on specific properties of extended-nano space, such as enhanced proton (H⁺) mobility and high Laplace pressure, and these new findings can be useful for H⁺ and H₂/O₂ separation [2].

In our previous work, we developed the device structure of light-driven H₂/O₂ generation chip [3]. Also the working principle was verified and proved our basic concept of H₂/O₂ generation and the gas-liquid separation under light illumination. However, the incident photon to current efficiency (IPCE) under 0.5 V bias and UV light illumination was 0.016 %, which was approximately 500 times lower than conventional photocatalytic water splitting in bulk. The reasons for low IPCE are TiO₂ photoanode structure and the integration method. To improve the performance, we have to develop a new photoanode structure and also new strategy for the chip fabrication method for efficient water splitting.

In this paper, we report on the fabrication of TiO₂ nanorods structure and on the new technologies to integrate the photocatalytic system in the microchip. The evaluation of the photocatalytic water splitting and the gas-liquid separation are also discussed.

PRINCIPLE

To achieve the photocatalytic H₂/O₂ generation and separation in the micro-space, we proposed the structure of the chip which is shown on Fig.1. The proposed concept consists of three parts: (1) photocatalytic water splitting system, (2) H⁺ transfer and H₂/O₂ separation system, and (3) gases separation system. For part (1), TiO₂ photoanode and Pt cathode are integrated into the microchannels. The microchannels (in part 2) are bridged by extended-nano channels (400 nm wide, 200 nm deep), and finally the shallow micro channels which are located to parallel deeper micro channels (see Fig.1) are partially modified by fluoropolymer solution for part (3), the gas-liquid separation [4].

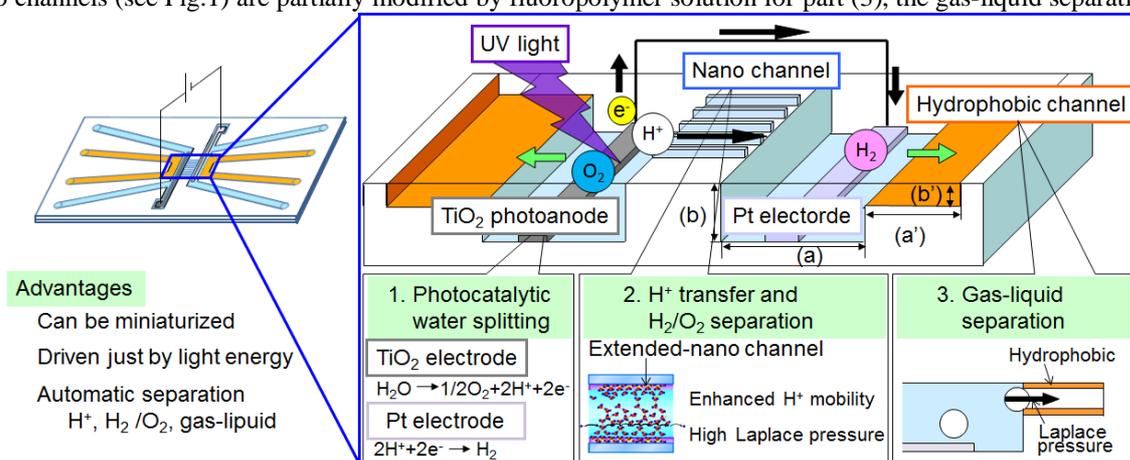


Figure 1: The concept of the H₂/O₂ generation chip. ($a=600\mu\text{m}$, $b=7\mu\text{m}$, $a'=400\mu\text{m}$ and $b'=1\mu\text{m}$).

When the photoanode is illuminated by the solar light, water can be photocatalytically decomposed to O_2 , H^+ and e^- . Proton is transferred to Pt cathode through the extended-nano channels and then H_2 is catalytically produced. On the next step, the generated gases are separated with help of hydrophobic shallow micro channels. During these processes, the generated gases cannot be introduced into the extended-nano channels due to high Laplace there. In our previous work [3], we already reported on details of the working principle of proposed device. However, IPCE value under UV illumination and 0.5 V bias was quite low. The first problem is chip fabrication method. The chip is made of two fused silica substrates that are bonded each other at 1080 degree celsius which leads to the damage of TiO_2 photoanode and decreasing photocatalytic activity. The second problem is the conductive layer of photoanode. At previous work [3], we utilized Pt for conductive layer, however the Schottky barrier occurred between the Pt and the TiO_2 layer which resulted interferes of the electron transfer. To overcome these problems and to achieve the efficient photocatalytic water splitting, we developed new TiO_2 nanostructured photoanode and new chip fabrication methodology.

EXPERIMENT

The fabrication process of TiO_2 photoanode (which is based on brush type TiO_2 nanorods structure) is shown in Fig. 2, and it was realized by the combination of the Glancing Angle Deposition (GLAD) and the anodic anodization techniques, respectively. In the GLAD regime, the angles measured between the substrate normal and the direction of incident flux are typically bigger than 80° . Therefore atoms that have already been deposited on the substrate create shadows behind them and shields that area from other incident atoms. The shadowing effect and limited atom diffusion eventually produce a nanostructure of small isolated columns slanting toward the incident beam [5]. After

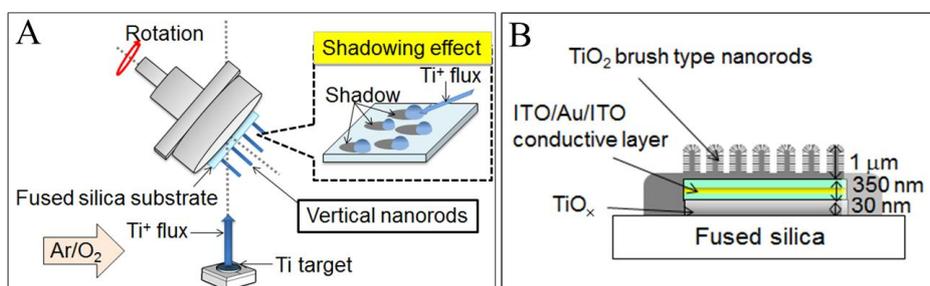


Figure 2. Fabrication of TiO_2 brush type nanorods. (A)GLAD principle and (B) structure of new photoanode.

the integration of Ti nanorods on the conductive ITO-Au/ITO layer (which is located in microchannel), the sample was anodized and later TiO_2 brush type structure was converted into anatase structure by the annealing process at $450^\circ C$.

Then, we utilize the low temperature bonding (at $100^\circ C$) [6] and fabricate the new H_2/O_2 generation chip (see Fig.3). After the chip fabrication, we performed two kinds of experiments to demonstrate the improvement and the working principle. The experimental setup is on Fig. 4.

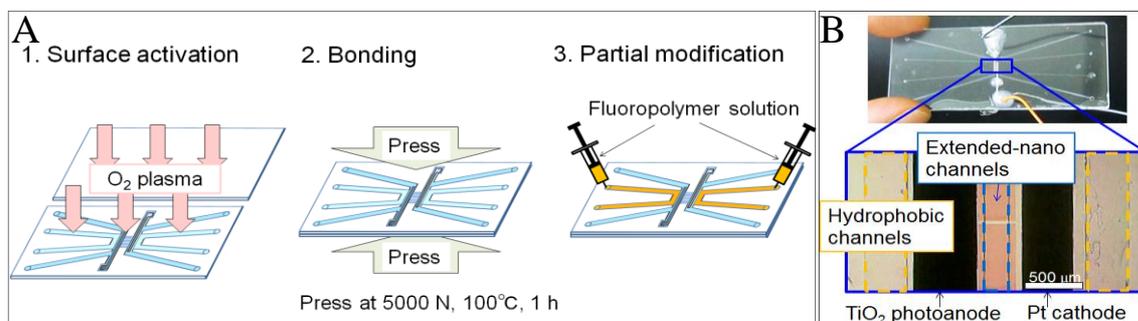


Figure 3. Low temperature bonding.(A) The protocol of chip fabrication (low temperature bonding and partial modification).(B) Snap shot of fabricated chip.

The photoelectrochemical performance of the fabricated chip was evaluated using a three-electrode configuration with TiO_2 brush type nanorods as photoanode, $Ag/AgCl$ as reference electrode and Pt as the working electrode. As electrolyte $NaClO_4$ aqueous solution (0.5mol/L) was introduced into the channels except hydrophobic microchannels. The potential and photocurrent of photoelectrode were controlled by a potentiostat. At first, we observed H_2/O_2 generation and separation under UV light and bias voltage (0.25 V vs $Ag/AgCl$ reference electrode) through a microscope. To evaluate the photoelectrochemical performance of the chip, we measured the photocurrent under the solar light simulator (PEC-L01, Peccell Tech. Inc., Japan).

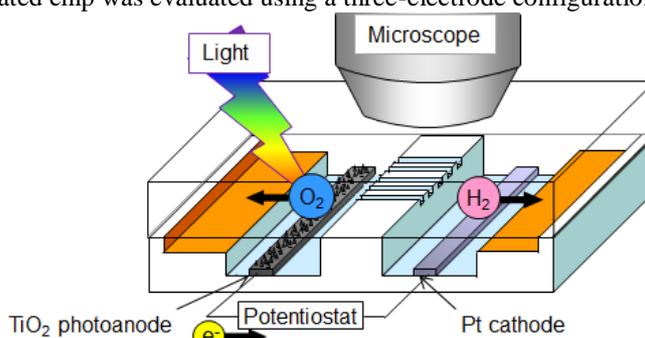


Figure 4. Experimental setup for photoelectrochemical measurement.

RESULTS AND DISCUSSION

The results of the H_2/O_2 generation and separation are shown on Fig. 5. Under 0.5 V bias and UV light ($\lambda=365$ nm, 86 mW/cm²), we observed the H_2/O_2 generation and separation. During the light illumination, H_2 and O_2 gases bubbles were formed on the surface of Pt cathode and TiO_2 photoanode, respectively. When the bubbles grow and reached the edge of the shallow hydrophobic channels, they are separated to the shallow hydrophobic channel due to Laplace pressure which enhance the gas introduction but prevent the water introduction to hydrophobic channel. These results clearly indicate the gases generation and separation driven by UV light illumination.

In next step, the working principle of the microchip has been verified under the solar light

illumination by measuring the generated photocurrent and result is present on Fig. 5. When the light is on, the photocurrent jump to the value about 60 $\mu A/cm^2$ and late it is saturated and stabilized in constant value about 35 $\mu A/cm^2$.

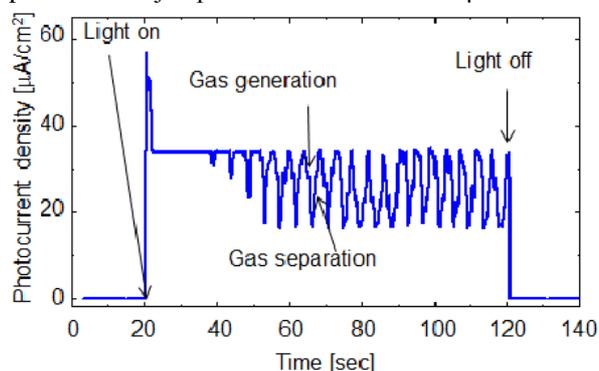


Figure 6: Photocurrent under solar simulator.

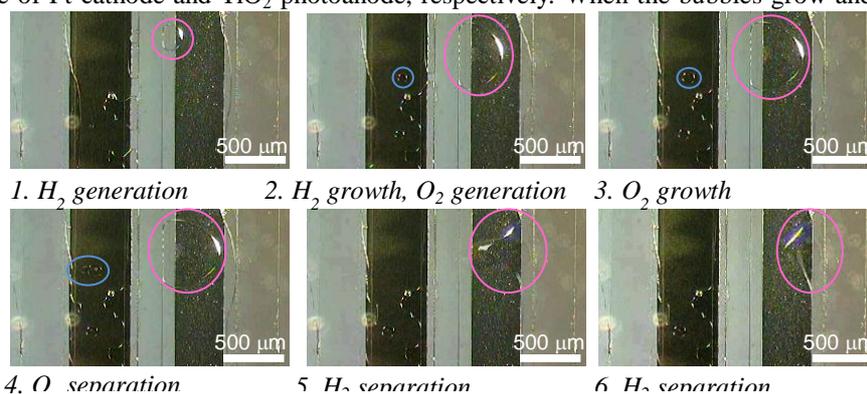


Figure 5. Snap shot of H_2/O_2 gas generation and separation.

After 40 seconds of illumination, the photocurrent value periodically started to sweep. This sweeping characteristic can be explained by the gas generation and the separation. When the gas bubbles are generated, the bubbles cover the electrode (see Fig. 4) and interfere the reaction, which resulted in the photocurrent decreasing. When the bubbles are removed from electrode, the photocurrent increased again. We also measured the IPCE under UV region and the maximum value $\sim 12\%$ was reached, which is around 750 times higher compared to the our previous work [3], and ~ 1.5 times higher than reported value for the bulk experiments based on TiO_2 flat film.

CONCLUSION

In this work, we developed new TiO_2 brush type nanorods structure and successfully integrated it into the micro device in form of photoanode for efficient H_2/O_2 generation. With our new TiO_2 photoanode and chip fabrication methodology, H_2/O_2 generation and the separation under the solar light illumination was demonstrated for the first time. From these results, we can conclude that we have established the new fabrication method of the light-driven micro fuel cell for efficient photocatalytic H_2/O_2 generation.

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