A novel photoelectrochemical cell with self-organized TiO$_2$ nanotubes as photoanodes for hydrogen generation

Yongkun Li$^{a,b}$, Hongmei Yu$^a$,*, Wei Song$^a$, Guangfu Li$^{a,b}$, Baolian Yi$^a$, Zhigang Shao$^a$

$^a$Laboratory of Fuel Cells, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 457 Zhongshan Road, Dalian 116023, PR China
$^b$Graduate University of Chinese Academy of Sciences, Beijing 100039, PR China

A photoelectrochemical (PEC) cell with an innovative design for hydrogen generation via photocatalytic water splitting is proposed and investigated. It consisted of a TiO$_2$ nanotube photoanode, a Pt/C cathode and a commercial asbestos diaphragm. The PEC could generate hydrogen under ultraviolet (UV) light-excitation with applied bias in KOH solution. The Ti mesh was used as the substrate to synthesize the self-organized TiO$_2$ nanotubular array layers. The effect of the morphology of the nanotubular array layers on the photovoltaic performances was investigated. When TiO$_2$ photocatalyst was irradiated with UV-excitation, it prompted the water splitting under applied bias (0.6 V vs. Normal Hydrogen Electrode, NHE). Photocurrent generation of 0.58 mA/cm$^2$ under UV-light irradiation showed good performance on hydrogen production.

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1. Introduction

Photoelectrochemical (PEC) water splitting has attracted significant attention in the past decades as a promising renewable energy source due to their low production cost and simple manufacturing process [1–7]. Since the early 1970s, Fujishima and Honda reported a single-crystalline TiO$_2$ semiconductor photoanode for photocatalytic decomposition of water under UV-excitation and an external bias for the first time [8], great efforts have been devoted to the development of photocatalytic hydrogen production technologies [9–14]. However, the practical applications are still difficult. The main difficulties can be attributed to the lack of effective photocatalysts and efficient photocatalytic reactors [15]. In photoelectrochemical water splitting for hydrogen generation, the ITO (indium-tin oxide)/FTO (F-doped SnO$_2$) glass or metal substrate-based photoanode and the Pt cathode are used and immersed in an aqueous solution especially in alkaline solutions [16–21]. Porous material, such as glass frit, is used as the separator in the cell compartment. The drawback is that such a cell design is only suitable for small scale experiments, and the use of three-electrode or two separated electrodes in an undivided cell, or in a one-compartment cell, can be very problematic due to less effective separation of the generated hydrogen and oxygen. The gaseous mixture is hazardous and brings collecting problems.

Recently, Kamat and co-workers have reported a hybrid fuel cell based on the polymer membrane electrode assembly (MEA) consisting of a P-25 TiO$_2$ photoanode, a Pt cathode, and a proton exchange membrane for the hydrogen production, and there have other literatures about the new PECs’ structure for hydrogen generation [9,22]. However, the photocatalyst casted onto the carbon paper or carbon cloth would be peeled easily after long time run. Therefore, it is not suitable for long-
term water splitting operations. Whereas, the TiO₂ nanotube arrays incorporated with the Ti meshes will avoid this issue. Furthermore, the ions can be transferred easily from the anode to the cathode through the openings of the Ti meshes while it is difficult for Ti foils. In the Ti meshes substrate system, the ions transfer distance is short, that the ions transfer to the counter electrode faster. Besides, the growths of titanium oxide tubes on the Ti foil/meshes will strengthen the adhesion of TiO₂ nanotube arrays to the substrate. This can be a great opportunity for their use in electrically enhanced photo processes in which the electrical contacts are crucial to obtain high efficiency [23].

In this paper, a novel PEC cell with an innovative design is proposed and investigated. The core of the PEC cell is an MEA incorporated with Ti mesh as the substrates of the photo-anode and Pt/C carbon paper as the cathode. The MEA serves as a compact but effective reactor for water splitting as well as an effective gas separator. A self-organized TiO₂ nanotube arrays around the whole Ti mesh with high stabilities in alkaline environments is employed as the photoanode. Besides, a detailed investigation of this photoanode applying on photoelectrolysis of water under illumination of UV light is carried out. As for this type of PEC cell, the driving force for the water electrolysis is the applied potential and light source. In this way, gases generated at each electrode can be separated, and the utilization of light can be improved in comparison with the traditional three-arm reactor.

2. Experimental section

2.1. Materials

All chemical reagents were commercially available, including ethylene glycol, ammonium fluoride (NH₄F, AR). The purity of the titanium meshes was 99.8%. A commercial Pt/C electrode (Pt/C anchored on the Toray TGP-H-60 carbon paper, Sunrise Power Co. Ltd.) with Pt loading of 0.4 mg/cm² was used as the cathode, and asbestos (pore diameter 160 nm, thickness 0.5 mm, SiChuan, China) was used as the diaphragm. The electrolyte was KOH solution (1 M, pH ≈ 13.6).

2.2. Photoanode preparation

Ti meshes (0.2 mm thick, 99.8% metal basis, Dexmet Co. Ltd.) with 58% porosity were used as starting material to obtain the TiO₂ photoelectrodes. Prior to anodization, the Ti mesh was ultrasonically cleaned and degreased in acetone and ethanol successively, followed by rinsing with deionized water and drying in an air stream. Anodization was performed in a two-electrode configuration with titanium mesh as the working electrode under constant potential (30 V) at room temperature (20 °C). A rectangle-shaped carbon electrode (thickness 2 mm, area 4 × 4 cm²) served as the cathode. The distance between the two electrodes was kept at 4 cm in all experiments. A direct current power supply (HY 1791-20S, YaGuang Electronics Co. Ltd.) was used as the voltage source to drive the anodization. The Ti mesh was anodized in the electrolyte (pH ≈ 6.2) with a mixture of ethylene glycol (97.5 wt%), H₂O (2 wt%) and NH₄F (0.5 wt%). During the first 2 min of the anodization, little bubbles were generated out of the surface of the titanium mesh and afterward less gradually. The colour of the titanium mesh changed from white to light purple and finally brown. In order to achieve different morphologies of nanotubular array layers, anodization time ranged from 4 h to 10 h. After oxidation, the anodized samples were properly rinsed with deionized water to remove the occluded ions, and then dried in an air oven. A subsequent annealing treatment, performed at 450 °C (heating rate of 2 °C/min) in air, was needed to transfer the amorphous structure into crystalline anatase.

2.3. Measurements

A field emission scanning electron microscope (FESEM; Hitachi, S-4800) was used to analyze the morphology of the nanotubes and X-ray diffraction (XRD) measurements were carried out by using an X’pert PRO (PAN-alytical) with a Cu Kα tube. Photoelectrochemical features of TiO₂ photoelectrode were tested in a three-arm reactor, in which the TiO₂ sample worked as the anode, a platinum grid worked as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode; all the values of potential in the text were referred to SCE. The light source was an 8 W Deuterium lamp; 1 M KOH solution was employed as the electrolyte. The effective photoactive area of the cell was 1.3 cm². A computer-controlled potentiostat (CHI760, CH Instruments Co. Ltd., China) was employed to control the external bias and to record the photocurrent. The samples were anodically polarized at a scan rate of 5 mV/s under the illumination, and the photocurrent was recorded.

2.4. Photocatalytic hydrogen generation from water

In our early patent [24], a PEC cell was described as Fig. 1. With the anode (TiO₂ nanotube) and the cathode (Pt/C carbon paper) on two sides of the asbestos diaphragm, the membrane electrode assembly (MEA) was pressurized between two stainless steel flow-field plates. There were parallel channels flow at the cathode side, and an open chamber with a 24 cm² quartz window at the anode side, which allowed the photocatalyst surface exposed to the light. Rubber rings were positioned in the cell as the sealing. A potentiostat (PARSTAT 2273,
Princeton) was employed to control the external bias and to record the photocurrent generated. A 300 W Xenon Lamp (Beijing Perfectlight Co. Ltd.) served as the light source and optical filters kept the UV light (365 ± 15 nm) intensity at 70 mW/cm². A peristaltic pump circulated 1 M KOH solution from a reservoir to the reactor chamber. The gas was analyzed by a gas chromatography (GC-14C, CHIMADZU).

3. Results and discussions

3.1. Characterization of the photoanode

Fig. 2 shows the FESEM image of the highly ordered titania nanotube arrays prepared by the electrochemical anodization in an electrolytic solution with 2 wt% water and 0.5 wt% NH₄F in ethylene glycol. As shown in Fig. 2a, the structure of the nanotube arrays prepared at 30 V for 4 h is well ordered with circular shape, whereas, the nanotubes prepared for 6 h, 8 h and 10 h are not well ordered and not exactly circular (Fig. 2b, c, d). It is also observed in Fig. 2 that the length of the titania nanotubes varies with the anodization time. The length of the titania nanotubes increases as the anodization time changes from 4 h to 8 h, but the length limits at 4 μm which does not continue to increase with longer anodization time. On the other hand, the pore diameter and the wall thickness of the titania nanotubes does not completely depend on the anodization time. In all the prepared titania nanotubes, most of them are straight and highly compact, however, some of them are slightly bent resulting from the strained environment. The most interesting phenomenon is the nanowire/belt structure (Fig. 2b, c, and d), that the TiO₂ nanowire/belt likes nanograss floating on the top of the nanotube arrays. The lower part of the nanotube arrays is straight and well ordered, while the top is with poor uniformity and floating at random orientation. The possible reasons of this phenomenon are as follows. Firstly, the nanotube wall thickness of the prepared TiO₂ arrays is not even that the corrosion happens on the weak point, while the nanotubular openings that are exposed for more time than the bottom parts are firstly corroded. Hence, it is speculated that the corrosion firstly happens on the weak point along the nanotubes. Secondly, when increasing the water content to 10 wt% in the electrolyte and keeping F⁻/C₀ constant and other conditions unchanged, the nanowire/belt structure does not appear, and the nanotubes is well ordered with circular shape. Therefore, it can be inferred that the water content is a key role on the formation of the nanowire/belt structure. F⁻ transfers faster in water than in ethylene glycol.

Fig. 2 – FESEM images of titania nanotubes prepared by electrochemical anodization in 2 wt% water + 0.5 wt % NH₄F in ethylene glycol at 30 V for (a) 4 h (b) 6 h (c) 8 h (d) 10 h.
glycol, and there are more F⁻ on the surface of the TiO₂ arrays in water than that in ethylene glycol which leads to the faster corrosive speed. Compared with the effect of the nanotube wall nonuniformity, the formation of nanograss’s structure is more sensitive to the water content in the electrolyte. This process is effective to produce highly ordered TiO₂ nanotube arrays with tunable morphology via changing the anodization conditions.

The nanotube arrays prepared at 30 V for 4 h using aqueous ethylene glycol and ammonium fluoride solution are selected for further investigation. The XRD patterns of the as-anodized titania nanotube arrays before annealing treatment shows only the amorphous structure (figure not included) in nature and are annealed to convert them into crystalline phases. A representative XRD pattern of TiO₂ nanotubes annealed at 450 °C for 2 h is shown in Fig. 3, which shows anatase phase except substrate titanium. However, the tube wall thickness varies a lot compared with the previous state. Obviously, it does not vary uniformly along the nanotubes. The possible reason is that the amorphous nanotube arrays have different dilatabilities during the phase transition.

3.2 Photoelectrochemical performance of TiO₂ photoanode

The titania nanotube arrays (effective photoactive area = 1.3 cm²) prepared at 30 V for 6 h in 2 wt% and 10 wt% water electrolyte are used as the photoanodes in a typical three-electrode system to evaluate the activity for water photoelectrolysis, respectively.

Fig. 4a shows the photocurrent response to the light. Photocurrent reaches 112 μA/cm² and 90 μA/cm² under excitation, respectively, even with low external bias. The current drops to zero when the light source is switched off. It indicates that the photogenerated charges can be separated effectively in the TiO₂ anode and the current generated is from photocurrent. It is worth to note that the photocurrent boosts from 90 μA/cm² to 112 μA/cm² (Fig. 4b) as the water content increases from 2 wt% to 10 wt% at the same condition. This phenomenon indicates that the photoexcited charges of the 10 wt% water sample are separated more effectively under the illuminated conditions.

The FESEM images of titania nanotubes prepared by electrochemical anodization in 2 wt% water (a) and 10 wt% water (b) +0.5 wt% NH₄F in ethylene glycol at 30 V for 6 h are showed in Fig. 5. As it is discussed previously, there is nanowire/belt formed on the top of the nanotubes during the preparation in the electrolyte of 2 wt% water. This nanowire/belt can be easily collapsed after calcinations. The collapsed nanowire/belt blocks the nanotubular openings and prevents the light passing through. As a result, it cannot absorb and utilize the sunlight efficiently. However, the openings of the TiO₂ nanotube arrays prepared in the electrolyte of 10 wt% water are well ordered and uniform, and the generated photocurrent is obviously higher than that in 2 wt% water system.
The photo conversion efficiency ($\eta$) of the photoanode which converts the light energy into chemical energy is calculated using the following equation:

$$\eta(\%) = \left( \frac{\text{total power output} - \text{electrical power output}}{\text{light power input}} \right) \times 100$$

where, $J_p$ = photocurrent density (mA/cm$^2$); $E_{rev}^0$ = total power output; $I_pE_{app}$ = electrical power input; $I_0$ = power density of incident light (mW/cm$^2$).

$E_{rev}$ is the standard reversible potential which is 1.23 V vs. NHE, and the applied potential $E_{app} = E_{meas} - E_{soc}$, where $E_{meas}$ is the electrode potential (vs. SCE) of the working electrode at which photocurrent is measured under illumination. $E_{soc}$ is the electrode potential (vs. SCE) of the same working electrode at open circuit conditions under the same illumination and in the same electrolyte. With the equation, $\eta$ of the photoanode using UV spectrum can be calculated as 2.6% (at $-0.5$ V vs. SCE, $J_p = 0.112$ mA/cm$^2$, OCP = $-0.8$ V vs. SCE, $I_0 = 4$ mW/cm$^2$). The OCP is the potential difference between the working electrode (anode) and the reference electrode (SCE) at equilibrium.

### 3.3. PEC cell performance

The principle of the PEC cell has shown in Fig. 1. Excitation of TiO$_2$ nanoparticles with UV-light leads to the electron-holes separation, most of them recombine again, and the rest can induce redox reactions. The excited electrons that promote to the unoccupied conduction band transfer to the cathode through an external circuit. The holes which stay at the valence band transfer to the interface of the electrode/electrolyte, and OH$^-$ is oxidized. (Equation (1)–(3)).

**Excitation** : $\text{TiO}_2 + h\nu \rightarrow e^- + h^+$  

**Photoanode** : $2h^+ + 2\text{OH}^- \rightarrow \frac{1}{2}\text{O}_2 + \text{H}_2\text{O}$  

**Cathode** : $2e^- + 2\text{H}_2\text{O}$ \rightarrow $\text{H}_2 + 2\text{OH}^-$  

The PEC cell with the TiO$_2$ photoanode is operated in the alkaline electrolyte under the applied potential. The TiO$_2$ nanotube photoanode is prepared by electrochemical anodization in 2 wt% water + 0.5 wt% NH$_4$F in ethylene glycol at 30 V, and the obtained nanotubes length was 3 µm with anodization time of 4 h.

Fig. 6 shows the photocurrent response of the PEC cell with TiO$_2$ electrode under UV irradiation during the on/off cycles under the potentiostatic mode. During on/off cycles of the illumination, the photocurrent reaches 0.58 mA/cm$^2$ and the current drops to almost zero without illumination. It indicates that the PEC cell has good photo-electricity properties. A 4-h experiment is performed under UV-illumination with bias potential of 0.6 V for the PEC cell for hydrogen production. Desaturated KOH solution (1 M) is cycled by a pump with constant rate through both the compartments of the PEC cell. The bubbles coming out of the cell are collected into a vessel. GC-14C gas chromatography is used to analyze the trapped gas and confirms it to be hydrogen. The photocurrent keeps a stable value (about 0.58 mA/cm$^2$) during the entire 4-h test. It indicates that the TiO$_2$ photoanode is stable enough to withstand the mechanical stress and shows no loss of photoactivity. During the 4-h operation,
the PEC cell with photoactive area of 10.08 cm² generates nearly 7.2 ml of hydrogen under the steady-state condition, so the hydrogen evolution rate of 0.178 ml/h cm² can be detected at the average current of 0.58 mA/cm². If we consider an average current of 0.58 mA/cm² flowing through the circuit, it would expect to observe H₂ formation at a theoretical rate of 0.25 ml/h cm² (at 15 °C). The observed H₂ evolution rate of 0.178 ml/h cm² accounts for 71% of the amount predicted on the basis of current flow. The discrepancy between the theoretical and observed yield is likely to originate from the H₂ collecting.

4. Conclusions

A novel PEC cell was constructed by using Ti mesh as the substrate of the photoanode and Pt/C carbon paper as the cathode, respectively. Compared with the typical three-arm reactor, it has many advantages. The Ti mesh was anodized to synthesize the self-organized TiO₂ nanotubular array layer. The effect of the morphology of the nanotubular array layers on the photovoltaic performances of the cell was investigated and the results indicated that the well ordered nanotubular array layer is a key factor to achieve high conversion efficiency in the PEC cell. The highest photocurrent density of the anodization TiO₂ nanotubes was about 0.58 mA/cm² with a H₂ evolution rate up to 0.178 ml/h cm². The designed PEC cell was effective for hydrogen production and was able to separate the evolved gases completely. The Pt/C carbon paper as the cathode rather than Pt foil minimized the catalyst loading, which was an important progress to cut down the cost of the PEC cell. Further works are essential to optimize the material and the structure of the cell, and the progress will be reported in the near future.

Acknowledgments

This work was financially supported by the National Natural Science Foundations of China (No. 20636060, No. 20876154). We also thank Dr. Jingying Shi, the Molecular Catalysis & In-situ Characterization Group, Dalian Institute of Chemical Physics, Chinese Academy of Sciences.

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