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Biophotofuel cell anode containing self-organized titanium dioxide nanotube array

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ABSTRACT

We made a biophotofuel cell consisting of a titanium dioxide nanotube array photosensitive anode for biomass decomposition, and a low-hydrogen overpotential metal, Pt, as the cathode for hydrogen production. The titanium dioxide nanotubes (TiO_2 NTs) were prepared via electrochemical oxidation of pure Ti in NaF solutions. Scanning electron microscopy was used to analyze the morphology of the nanotubes. The average diameter, wall thickness and length of the as-prepared TiO_2 NTs were 88 ± 16 nm, 10 ± 2 nm and 491 ± 56 nm, respectively. Such dimensions are affected by the NaF concentration and the applied voltage during processing. Higher NaF concentrations result in the formation of longer and thicker nanotubes. The higher the voltage is, the thicker the nanotubes. The photosensitive anode made from the highly ordered TiO_2 NTs has good photo-catalytic property, as can be seen from the test results of ethanol, apple vinegar, sugar and tissue paper decomposition under ultraviolet (UV) radiation. It is concluded that the biophotofuel cell with the TiO_2 nanotube photoanode and a Pt cathode can generate electricity, hydrogen and clean water depending on the pH value and the oxygen presence in the solutions.

1. Introduction

The breakthrough in the intersection of energy and environmental research is considered as one of the solutions to the future sustainability of the world. The global energy needs are driving new developments, such as solar energy conversion [1–3], waste recycling [4,5], hydrogen generation [6–9], biofuel generation [10] as alternatives for energy production. For example, photoelectrochemical systems for solar energy conversion were investigated [11]. Photocatalysis was applied for clean fuel, hydrogen, production [12]. The biophotofuel cell method has been used recently, because this is a cheap, easy way to harvest solar energy for clean fuel production. The ability to generate energy from waste and wastewater under the irradiation of solar rays, while cleaning the water for reuse and recycle has been a strong incentive to develop this technology [13–15].

Although using biophotofuel cells for hydrogen production has been proposed for a considerably long time [16–22], many problems remain to be solved. For example, Lambert and Smith have found that the efficiency of hydrogen production from the decomposition of marine blue-green algae is low [21]. This is because the performance of electrodes is not good enough. A lot of efforts have been put on exploring new functions and improving the efficiency of biophotofuel cells. Recent studies by Kaneko et al. found that both the quantum efficiency and hydrogen generation rate of biophotofuel cells can be increased using titanium oxide particle materials [23–25]. Antoniadou and Lianos showed that near UV and visible irradiations can decompose organic substances to generate electricity and hydrogen simultaneously [26].

The advantage of using nanomaterials especially nanoparticles has been justified based on the fact that nanoparticles have much higher surface areas than bulk materials [27,28]. TiO_2 nanoparticles have been shown to be potential candidates for biofuel generation [29]. Nevertheless, the agglomeration of particles is a challenging problem to be solved in order to keep the high surface area for different applications [30,31]. In our early work, we proposed two ways to solve the agglomeration problem based on the studies of nanoscale energy conversion materials [32,33]. The first way is to let nanoscale phases grow out-of-the-plane along some preferential directions to form nanoscale fractals or dendrites, which prevents the agglomeration of nanoparticles on substrates [32]. The other method is to use nanoporous substrates or templates because they can confine the growth of nanocrystals either inside the wall of the nanopores or on the surface of the substrates to prevent the agglomeration of nanoparticles [33].

In this work, self-organized anodic titanium dioxide nanotube arrays were prepared to make biophotofuel cell anode with high surface area and strong photosensitivity. It has been demon-

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strated that under UV radiation condition, the solutions made from biodegradable organic materials decompose at the titanium dioxide nanotube anode. Ethanol, apple vinegar, sugar and bath room tissue paper are the biomass solutions or biowastes for photo decomposition tests. When a low-hydrogen overpotential metal, Pt, was used as the cathode to form a biophotofuel cell, hydrogen production at the Pt cathode was observed. The open circuit voltage of the biophotofuel cell was measured and the dynamic response of the photosensitive anode to UV light was characterized.

2. Materials and experimental methods

2.1. Materials and instruments

Pure titanium (Ti) sheet with 0.5 mm thickness was used as the start material for making self-organized TiO_2 nanotube arrays. Sodium sulfate (Na_2SO_4) and sodium fluoride (NaF), both purchased from Alfa Aesar, were used to make the electrolytes for electrochemical oxidation of the titanium. Previous work suggests that this kind of electrolyte can be used to control the size and orientation of the nanotubes. For example, Macak et al. found that neutral NaF solutions can thicker the wall of the TiO_2 nanotubes [34] and Narayanan et al. showed that TiO_2 networks were obtained in Na_2SO_4 + NaF electrolytes [35]. Titanium oxide could dissolve more slowly in neutral or base solutions than in acids, which helps titanium oxide to self-organize into nanotubes in a controllable way. Consequently, electrolytes containing Na_2SO_4 and NaF may be used to tailor the size of the nanotubes. In this work, two electrolytic solutions were prepared using 1.0 M Na_2SO_4 and two different molar concentrations of NaF. Both solutions were made first using deionized (DI) water and adding NaF to 0.1 M and 0.3 M, respectively. The power supply for the electrochemical oxidation is a regulated DC power source, model HY5003 (0–50 V, 0–3 A). A Quanta 3D field emission scanning electron microscope (FESEM) was used for the nanotube morphology observation. The ultraviolet lamp was the UVL-21 (365 nm UV, 4 W, 0.16 A) which supplied the UV irradiation for biomass decomposition. The irradiation power on the biophotofuel cell anode was 40 mW/cm^2. A CHI 400A electrochemical workstation was used to monitor the biomass decomposition process and measure the hydrogen generation rate via chronocoulometry. A tubular type carbon dioxide sensor connected to an Xplorer GLX data acquisition unit was set up to measure the concentration of carbon dioxide associated with the biomass decomposition.

Diluted orthophosphoric acid (H_3PO_4) with the concentration of 20 wt.% was used for making biomass solutions. Four biomass solutions were used in this study. To make the first two types of biomass solutions, ethanol and tissue paper were dissolved into the diluted orthophosphoric acid, respectively. In one of the solutions, the concentration of H_3PO_4 is 10 wt.%, and the concentration of ethanol is 20%. In the other solution, the weight ratio of the tissue paper and the diluted H_3PO_4 is 1:1. The tissue paper was dissolved into the acid to form pulp. The other two biomass solutions are: 20% sugar solution and as-purchased apple vinegar from market with pH 0.8.

2.2. TiO_2 nanotube anode and biophotofuel cell fabrication

The 0.5 mm thick titanium (Ti) thin sheet was cut into 40 mm × 5 mm × 0.5 mm samples. Self-organized TiO_2 NTs were prepared by electrochemical oxidation of the Ti samples in the 1.0 M Na_2SO_4 + 0.1 M NaF electrolyte. Comparative studies were made using the solution containing 1.0 M Na_2SO_4 + 0.3 M NaF. A three-electrode cell was used for the electrochemical oxidation of Ti at room temperature of 25 °C. The anode and the cathode are

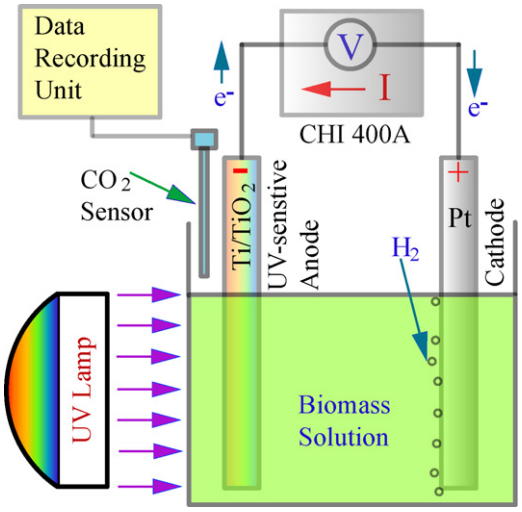

Fig. 1. Schematic of the biophotofuel cell with the TiO_2 nanotube anode and Pt cathode.

the Ti samples with the same size. The distance between the two electrodes was 20 mm. The operation voltage was 20.0 V and the electrochemical oxidation time was 90 min. After electrochemical oxidation, the samples were rinsed in deionized water and air dried. The surface of the anode was completely covered by TiO_2 nanotube arrays as revealed by the electron microscopic analysis. The biophotofuel cell (BPFC) was a one-compartment cell made of Pyrex glass, as schematically shown in Fig. 1. The anode was made from the TiO_2 nanotube arrays set on the Ti. The cathode was Pt. The main reaction at the cathode was hydrogen generation. Photoelectrochemical reaction occurred at the anode to decompose biomass and generate electron and carbon dioxide. Electricity was also generated at the same time.

In order to examine the formation mechanisms of the TiO_2 NTs, a solution with higher NaF concentration of 0.3 M was used to make NTs. Electrochemical processing at different maximum DC voltages including 5 V, 10 V and 20 V was performed to obtain TiO_2 NTs with different lengths and diameters. The dimension measurement results were used for statistic analysis to obtain the size distribution plots.

3. Results and discussion

3.1. Surface morphology of the TiO_2 nanotube photoanode

Fig. 2 shows the surface morphology of the anode with TiO_2 nanotube arrays. Fig. 2(a) is a low magnification scanning electron microscopic (SEM) image, from which the porous surface can be seen. At higher magnification, the nanotubes are shown in Fig. 2(b). Fig. 2(c) reveals many separated nanotube bundles. At even higher magnification, as shown in Fig. 2(d), it can be seen that the TiO_2 nanotubes have a diameter of about 88 nm. The wall thickness is about 10 nm. If the electrochemical oxidation parameters such as voltage and time were changed, the size of the TiO_2 NTs can be changed, which was also reported by other researchers using different electrolytes consisting of HF or NH_4F [36,37]. Energy dispersive X-ray spectrum was obtained using the same Quanta 3D field emission scanning electron microscope (FESEM). The analyzed region is shown in Fig. 2(e) and the result is shown in Fig. 2(f), which reveals Ti and O are the major elements at the anode. Quantitative analysis gives the atomic ratio of Ti:O = 1:2, which means that the nanotubes have the stoichiometric composition of titanium dioxide. The weight percentage of each element is shown in the inset in Fig. 2(f). The weight ratio is Ti:O = 3:2.