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A cascading gradient pore microstructured photoanode with enhanced photoelectrochemical and photocatalytic activities

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ABSTRACT

In this work, a novel photoanode with a cascading gradient pore microstructure is proposed to enhance photoelectrochemical and photocatalytic activities, which consists of a nanocrystalline TiO_2 layer synthesized by the sol–gel method, a microporous layer, and a macroporous layer formed by adding PEG and PMMA as the template, respectively. The gradient pore microstructure can not only enhance the mass and photon transfer and improve the light utilization, but also increase the electrical conductivity and restrain the recombination of photoexcited electron–hole pairs. Furthermore, the cascading design helps to establish tighter interparticle connections between layers. Because of these merits, it has been found that the cascading gradient pore microstructured photoanode exhibited a 63% improvement over the conventional photoanode in terms of photoelectrochemical activity. This new design also enhanced the photocatalytic activity, leading to a much higher methylene blue degradation efficiency (76.7%) than that of conventional photoanodes (62.5%). The effect of the PMMA/TiO_2 ratio on the structure and performance of the proposed photoanode was also investigated. The highest performance was achieved with a PMMA/TiO_2 ratio of 1:1. The obtained results establish a new avenue for designing the photoanodes of photoelectrochemical systems.

1. Introduction

As one of the typical photoelectrochemical systems, photocatalytic fuel cells (PFCs) that integrate photocatalytic oxidation and fuel cell technologies have become an advanced research area in recent years [1–4]. Upon illumination, photosensitive semiconductors at the photoanodes of PFCs generate electron–hole pairs with photonic energy greater than their band gap. Photoinitiated holes that have strong oxidation ability are then able to degrade most organics, while electrons flow to the counter electrode to generate electricity. In this way, the chemical energy contained in energy-rich wastewater can be recovered to provide energy along with organic contaminant degradation. Therefore, PFCs have the potential to alleviate both energy shortages and environmental contamination issues facing our planet by degrading pollutants and simultaneously generating electricity [5]. Moreover, PFCs feature wild operation conditions, low secondary pollution, and easily controlled reactions, making them a promising application prospect [6–9].

At present, TiO_2 is the most widely used PFC as a photocatalysts due to its high activity, nontoxicity, low cost, and chemical inertness [10]. To prepare the photoanodes, TiO_2 is usually given in the form of a thin film by applying TiO_2 to conductive glass via various methods [11–13], such as the screen-printing method, doctor-blade technique, and wet spraying method. However, the TiO_2 films formed by these methods often exhibit low specific surface area and poor photon and mass transfer, which strongly constrain its photoelectrochemical and photocatalytic activities. To address this problem, much effort has been undertaken to ameliorate the spatial structure of the photoanode [14,15]. One common method is the in situ growth of TiO_2 nanorods, nanotubes, nanowires, etc. [16–18], which have been found to be able to dramatically improve the specific surface area and mass transfer. For instance, Liu et al. [19] prepared a short TiO_2 nanotube array and applied it to PFCs. Compared with conventional TiO_2 films that were stacked by TiO_2 nanoparticles, the nanotube-array structure demonstrated improved photoelectrochemical performance. However, the in situ growth of TiO_2 is usually conducted on a Ti-based substrate. This is difficult to realize on conductive glass and also complicated

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for manufacturing. Another approach to ameliorating the spatial structure of the photoanode is to construct porous TiO_2 films using polystyrene (PS), poly(methyl methacrylate) (PMMA), octadecylamine (ODA), or other microspheres as templates [20]. In 2010, Kamegawa et al. [21] successfully prepared a TiO_2 film with uniform pores using PMMA as the template. As compared with traditional dense TiO_2 film, it was found that this porous structure provided superior photocatalytic degradation efficiency to 2-propanol and acetaldehyde. Zhang and Bai [22] utilized ODA as the template to synthesize a porous TiO_2 film by a sol–gel method and confirmed that this porous structure was superior in methyl orange degradation. However, although these porous TiO_2 films have shown good performance in photocatalytic wastewater treatment, when they were applied to the glossy surface of the conductive glass that was commonly used as the photoanode substrate of PFCs, they could be easily peeled off due to the voids and shrunk contact area with the substrate [23]. In short, it is important to develop a high-efficiency photoanode for improving PFC performance.

It is known that complicated multiple processes are involved in the photoanode, including photon receipt, electron–hole pair generation, and mass and photon transport. A high-efficiency photoanode should have the following features: large specific surface area, high mass transfer efficiency, and effective electron transfer pathways, along with improved photon transfer ability for light harvesting and strong adhesion to the conductive substrate. However, the existing photoanodes, especially those with a single-layer structure, cannot easily fulfill these requirements, because the single-layered compact TiO_2 film has small specific surface area and poor mass transfer ability, and the single-layered porous TiO_2 film has a poor connection to the conductive substrate and thus inferior electrical conductivity. Therefore, to overcome the drawback of the single-layer structure, a novel multilayer photoanode with a cascading gradient pore microstructure is proposed in this work. As illustrated in Fig. 1, the cascading-gradient-pore microstructured photoanode consists of three layers on the FTO conductive glass: a nanocrystalline TiO_2 layer at the bottom, a microporous TiO_2 layer in the middle, and a macroporous TiO_2 layer on the top. Such a cascading-gradient-pore microstructure offers the following desired features for the photoanode. First, the top macroporous TiO_2 layer provides sufficient light-transfer path and facilitates light scattering, thus allowing incident photon flux to be absorbed efficiently. In addition, it can also provide large specific surface area for the photoelectrochemical reaction and small transport resistance for facilitating the mass transfer of organic fuels and ions. The middle microporous TiO_2 layer can not only provide efficient diffusion pathways for mass transfer but also help to trap the incident photons. The bottom nanocrystalline layer ensures strong adhesion to the electrode substrate, provides high conductivity, and prevents the recombination of photoexcited electron–hole pairs. Furthermore, the cascading design can avoid direct contact between two layers with large pore size difference, helping to establish tighter interparticle connections between these layers and enhancing the electron transport from the external porous network structure to the internal electrode substrate. All these features of this novel photoanode will enhance its performance.

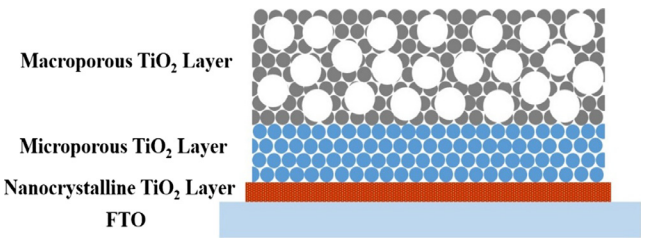

Fig. 1. Schematic of the cascading-gradient-pore microstructured TiO_2 photoanode.

We developed this novel photoanode layer by layer. From the bottom to up, the three layers with different pore structures were fabricated successively onto the FTO conductive glass. (i) A nanocrystalline TiO_2 layer was first deposited on the FTO conductive glass by the sol–gel method, termed NC-TiO_2. (ii) A microporous TiO_2 layer was then fabricated on the top of the nanocrystalline TiO_2 layer by the wet spray method using polyethylene glycol (PEG) as a template to form micropores, termed Micro-TiO_2. (iii) Finally, a macroporous TiO_2 layer was formed on the top by spraying the TiO_2 colloid with the addition of a poly (methyl methacrylate) (PMMA) template (1.8 μm in diameter) to form macropores, termed Macro-TiO_2. In this way, a novel photoanode with a cascading gradient pore microstructure, termed NC-TiO_2/Micro-TiO_2/Macro-TiO_2, could be developed. Both the photoelectrochemical and photocatalytic activities of the fabricated novel photoanode were evaluated. The role of each layer in this design was further elaborated. In particular, the effect of the TiO_2/PMMA ratio on the structure and performance of the developed photoanode was also investigated. Results showed that this novel photoanode could greatly enhance the photoelectrochemical and photocatalytic activities, which provides a potential direction for the development of the photoanode.

2. Materials and methods

2.1. Preparation of the photoanode

The cascading-gradient-pore microstructured photoanode, which consisted of a nanocrystalline TiO_2 layer at the bottom, a microporous TiO_2 layer in the middle, and a macroporous TiO_2 layer on the top, was prepared on FTO conductive glass. The bottom densely packed nanocrystalline TiO_2 layer was first synthesized by the sol–gel method onto FTO conductive glass cleaned by sonication in acetone, isopropanol, and ethanol. The procedure was as follows [24]: 3.5 g of the nonionic surfactant Triton X-100 (Sigma-Aldrich, USA) was first mixed with 19 mL of ethanol. Then 3.4 mL of glacial acetic acid (Aladdin, China) and 1.8 mL of titanium tetraisopropoxide (Aladdin, China) were added with vigorous stirring. After stirring, the prepared colloid was applied to the FTO conductive glass by dipping, dried in air for a few minutes, and finally calcined at 550 °C for 10 min with a temperature ramp of 20 °C min^{-1} to form a nanocrystalline TiO_2 layer. On the top of the nanocrystalline layer, the microporous layer was formed by wet spraying with the TiO_2 colloid. The TiO_2 colloid was prepared by the conventional sol–gel method [25], in which 6 g of TiO_2 nanoparticles (Aeroxide P25, Acros, Belgium) were dispersed in a mixture of 60 mL DI, and 0.1 mL of a Triton X-100 (Sigma-Aldrich, USA) and 1.2 g polyethylene glycol (PEG2000, Aladdin, China) were added and mixed for 12 h. The prepared TiO_2 colloid was then diluted with ethanol and applied on top of the nanocrystalline TiO_2 layer by an air spray gun. The TiO_2 loading of the microporous layer was kept at 0.2 mg cm^{-2}. The top macroporous TiO_2 layer was prepared using TiO_2 colloid and PMMA microspheres with 1.8 μm in diameter (Soken Chemical and Engineering Co., Japan) as a template. The PMMA microspheres were added into the TiO_2 colloid. First, 2.5 g of PMMA microspheres were dispersed in 20 mL of distilled water containing 6 wt.% of polyvinyl alcohol (PVA, Aladdin, China) and then they were stirred at 95 °C in an oil bath for 2 h. After that, the prepared PMMA aqueous solution was introduced into the TiO_2 colloid in various proportions. After 24 h of stirring at room temperature, the resulting suspension was deposited onto the substrate by wet spraying. After drying