Applied Surface Science 458 (2018) 382–388

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Full Length Article

Enhanced photoeletrochemical biosensing performance from rutile nanorod/anatase nanowire junction array

Bingdong Yan[a], Yi Zhuang[a], Yulin Jiang[a], Wei Xu[a], Yongjun Chen[a], Jinchun Tu[a], Xiaohong Wang[a,*], Qiang Wu[b,*]

[a] State Key Laboratory of Marine Resource Utilization in South China Sea, Key Laboratory of Tropical Biological Resources of Ministry of Education, Hainan University, Haikou 570228, PR China

[b] Laboratory of Tropical Biomedicine and Biotechnology, School of Tropical Medicine and Laboratory Medicine, Hainan Medical University, Haikou 571199, PR China

ARTICLE INFO

Keywords:
R/A-TiO_2 heterostructure
Glucose oxidase
PEC biosensor

ABSTRACT

In this work, a novel enzymatic glucose photoelectrochemical biosensor was successfully fabricated based on rutile/anatase TiO_2 (R/A-TiO_2) heterostructure which was composed of anatase nanowires and rutile nanorods. Compared to a rutile nanorod electrode, an obvious enhanced photocurrent was observed on R/A-TiO_2 electrode in photoelectrochemical test. Excellent photoeletrochemical performance was obtained due to these follow points: higher optical absorptivity for the larger surface area, better separation of the photogenerated carriers related to the specific R/A-TiO_2 heterostructure and faster electrical transmission stemmed from the unique conductive structure. This R/A-TiO_2 heterostructure array was applied to glucose detection by loading glucose oxidase on R/A-TiO_2 electrode. A remarkable performance with a 5.71 $\mu A\,mM^{-1}\,cm^{-2}$ sensitivity, 1–20 mM linear range and a 0.019 mM glucose detection limit (S/N = 3) were obtained in the glucose detection.

1. Introduction

In recent years, photoelectrochemical (PEC) biosensors have emerged as a new promising analytical tool in biological and biochemical assays due to their synergistic advantages from electroanalytical and photocatalytic methods [1]. PEC systems possess a unique signal transducing modality refer to separate processes of signal generation (photo) and detection (electrochemical) [2]. The PEC sensors have attracted widespread attention for their low background signals, inherent miniaturization, portability and easy automation [3]. The emergency of new PEC materials does not hinder researchers' enthusiasm on TiO_2 who own favorable conduction band edge, finer stability, and low cost characters [4]. Therefore, arious morphologies of TiO_2 were applied to PEC system.

1D TiO_2 nanorods are excellent candidate for photoelectrochemical biosensor because its fast electronic transmission capability could reduce recombination of photo-generated electron hole pair [3]. 1D TiO_2 nanorod arrays in situ grown on various transparent conductive substrates, are endowed with numerous advantages such as a large surface area, fast charges transport, and ameliorated light absorption in virtue of scattering [5]. A method developed by Liu and Aydil has become one of common method to prepare the rutile TiO_2 nanorod (NR) arrays on fluorine-doped tin oxide (FTO) substrates [14]. This procedure not only offered intimate contact between TiO_2 nanorod arrays and the FTO substrate but also led to the formation of a direct pathway for the photogenerated electrons to reach the electron collector. However, the poor charge separation is the fatal drawback of single-phase TiO_2 nanorod arrays [6]. Obviously, further efforts are still indispensable to suppress the recombination of electron and hole.

According to previous research results [7–9], coupling two different semiconductors together could improve interfacial charge separation because of their discrepant band-edge positions and band gaps. Incorporating anatase and rutile, the two most common TiO_2 phase used in PEC application, would suppress the charge recombination so that the photocatalytic ability could be strengthened [10]. By employing this strategy, brilliant performance has been acquired in different fields, such as water-splitting [11], solar cell [12] and photodetector [13]. The conduction band of rutile TiO_2 is usually lower than that of anatase TiO_2 while their valence bands are similar. This energy discrepancy could be the driving force for carriers separation. When illumination happened to rutile/anatase TiO_2 heterojunction, the photogenerated electron could flow from the conduction band of anatase TiO_2 to that of rutile TiO_2.

Herein, a novel PEC biosensing platform by entrapping glucose

* Corresponding authors.
E-mail addresses: wangxiaohong@hainu.edu.cn (X. Wang), wuqiang001001@aliyun.com (Q. Wu).

https://doi.org/10.1016/j.apsusc.2018.07.088
Received 30 March 2018; Received in revised form 9 July 2018; Accepted 11 July 2018

oxidase on R/A-TiO_2 heterostructure (R/A-TiO_2@GOx) was synthesized. It is large surface area and special hierarchical structure that make the enzyme much easier to be loaded. Both advantageous electron transport path and logical heterostructure make the electron easier to be transferred to electrode. Compared to single crystal TiO_2 nanorod arrays, the R/A-TiO_2 exhibited a better PEC biosensing performance with a remarkable sensitivity (5.71 μA mM^{-1} cm^{-2}) a wide response range (1–20 mM) and a low detection limit (0.19 mM).

2. Experimental methods

2.1. Materials and reagents

FTO glasses were purchased from Outhwaite New Energy Company. Tetrabutyl titanate ($C_{16}H_{36}O_4Ti$), titanium oxalate ($K_2TiO(C_2O_4)_2$) and diethylene glycol (DEG) were acquired from Shanghai Sinopharm Chemical Reagent Company. Hydrochloric acid (HCl), urea (H_2NCONH_2), ethanol (CH_3CH_2OH) and glucose ($C_6H_{12}O_6$) were obtained from Guangzhou Chemical Reagent Factory. Glucose oxidase (GOx) was gained from Shanghai Bioengineering Co. Ltd. All materials were used as received without any further purification.

2.2. Preparation of R-TiO_2 nanorods crystal arrays

The R-TiO_2 nanorods arrays were grown on FTO glass employing the typical method reported by Liu and Aydil [14]. 50 mL deionized water with 50 mL concentrated hydrochloric acid were poured together to prepare a dilute hydrochloric solution. After being stirred 5 min at ambient temperature, 400 μL tetrabutyl titanate ($C_{16}H_{36}O_4Ti$) was added into the mixture. Afterwards, this mixture was transferred into a Teflon-lined stainless steel autoclave. Then, the FTO substrates were ultrasonically cleaned with ethanol and water, respectively. After that, FTO substrates were placed at the Teflon and make sure the substrates had appropriate angle against Teflon wall and conductive side facing down. After 10 h heated at 150 °C, the autoclave was cooled down to room temperature naturally. Next, the substrates were taken out and washed with distilled water. At last, the obtained substrates above were annealed in air atmosphere at 400 °C for 2 h to heighten the crystallinity.

2.3. Preparation of R/A-TiO_2 arrays

A-TiO_2 nanowires were synthesized via a simple hydrothermal method. Typically, 10 mL of deionized water and 30 mL of diethylene glycol (DEG) were mixed in a 50 mL Teflon-lined stainless steel autoclave. Then, 0.35 g $K_2TiO(C_2O_4)_2$ and 0.5 g urea were added to the mixture solvent vigorous stirring until system became homogeneous. The substrates above was placed into the Teflon-lined stainless steel and the container was annealed at 180 °C for 2 h. Following, the samples were washed with ethanol and water and then dried in an oven at 80 °C overnight. Finally, the samples were heated to 500 °C for 2 h in Ar atmosphere.

2.4. Fabrication of the PEC electrode

To prepare the R/A-TiO_2@GOx biosensor, the R/A-TiO_2 FTO electrode was successively rinsed for 30 min with acetone, ethanol and ultrapure water under ultrasonication, and dried at room temperature. Meanwhile, 10 μL of aqueous GOx solution (10 mg mL^{-1}) containing 10 μL Nafion (1% w/w) was prepared, the mixture was agitated in a thermostatted oscillator at 4 °C for 4 h. Finally, 20 μL of this mixture was applied on the R/A-TiO_2 FTO electrode dried at 4 °C for 8 h. For comparison, the A-TiO_2@GOx FTO electrode was also fabricated in the same procedure.

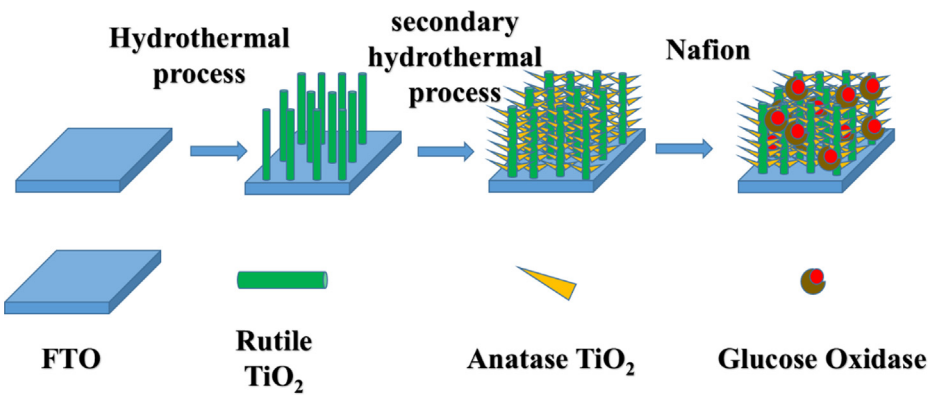
2.5. Instruments and measurements

The surface morphology of PEC electrode was characterized using a field emission scanning electron microscope (FESEM, Hitachi SU8010). The TEM images were acquired on a transmission electron microscopy (JEOL JEM 2100). The UV–vis absorption spectrum was collected on a UV–vis absorption spectrophotometer (JASCO, UV-550) from 300 to 800 nm. Fourier transform infrared (FTIR) spectra were recorded (1486.6 eV) on a Bomem MB 100 FT-IR spectrometer (ABB Bomem, QC, Canada) in the wavenumber range between 400 and 4000 cm^{-1}. PEC tests were performed by a CHI 660C workstation (CHI Instruments, Chenhua, Shanghai, China) equipped with 500 W Xenon lamp. Conventional three-electrode electrochemical system was employed in PBS buffer (pH = 7.4) electrolyte at room temperature, in which R/A-TiO_2@GOx electrode was employed as working electrode, while Ag/AgCl served as reference electrode and Pt foil as counter electrode. The distance between Xenon lamp and electrolytic cell is about 30 cm.

3. Results and discussion

3.1. Preparation of PEC electrode

The synthesis procedure of the R/A-TiO_2@GOx FTO electrode for the PEC sensor of glucose is illustrated in Scheme 1. Firstly, R-TiO_2 was prepared by hydrothermal process according to the literature method. After that, the anatase TiO_2 was grown on R-TiO_2 in a secondary hydrothermal process. Then, GOx was successfully modified on the R/A-TiO_2 nanoarrays with the assistance of Nafion. Finally, a PEC system for glucose detection by decorating GOx on the R/A-TiO_2 heterostructure arrays was successfully fabricated.



Scheme 1. The process to fabricate the R/A-TiO_2@GOx biosensor.