Supplementary Information

High performance of Membraneless and Mediatorless Glucose/Air Biofuel Cells Introducing photoanode with TiO_2 Nanotubes

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Experimental Section

Chemicals. Titanium foil (purity > 99.7%) was purchased from Aldrich. Bilirubin oxidase (BOD) (E.C. 1.3.3.5, initial activity of 18 U/mg, from Myrothecium verrucaria) was obtained from Sigma. Hydrofluoric acid, nitric acid, acetone, absolute ethanol and β-D-(+)-glucose were of analytical grade from Beijing Chemical Reagent Company (China) without further purification. Multiwall carbon nanotubes (CNTs) were purchased from Shenzhen Nanotech. Port. Co. Ltd. (Shenzhen, China) without further purification. 1-Butyl-3-methylimidazolium hexafluorophosphate ([bmim]PF_6) (IL) was purchased from J&K Chemical LTD. without pretreatment. Glucose stock solution was kept for 24 hours before use. Ultrapure water from Water Purifier (Sichuan Water Purifier Co., Ltd., China) was used in all the experiments.

Preparation of TiO_2 nanotubes (TNTs) photoanode. The ordered TiO_2 nanotubes were prepared by a potentiostatic anodization in a two-electrode electrochemical cell. A 0.25-mm-thick titanium foil with a size of 0.5 cm × 0.5 cm was used as a working electrode, and a platinum foil with the same size served as a counter electrode. The interval between working electrode and counter electrode was about 2 cm. Prior to anodize, the titanium foil was chemically etched by immersing in a mixture of HF and HNO_3 (volume ratio of HF:HNO_3:H_2O in 1:4:5) for 40 s. Then the titanium foil was

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rinsed with acetone, absolute ethanol and water for 10 min, respectively. The substrate was then dried in air at room temperature. The voltage was applied by a DC power supply (SK1730SL1A, Sanke Technologies). The TiO_2 NTs were formed by anodizing the Ti foil in 40 mL of 0.5 wt% HF solution at 20 V for 20 min with magnetic agitation, which is the same as the reported method.[1] During anodization, the color of the titanium oxide layer normally changed from purple to blue, light green, and then finally light red. Anodized titanium foils were annealed in at 500 °C for 3 h in air atmosphere, heating and cooling rates were kept at 1 °C min^{-1}.

Preparation of BOD/CNTs-IL/GCE biocathode. CNTs-IL nanocomposite was prepared via the same procedure as in our previous work. Briefly, 2 mg CNTs and 20 μL IL were ground for about 15 min in an agate mortar to form a viscous gel. Glassy carbon electrode (GCE, 3 mm in diameter) was polished with 1.0 and 0.3 μm alumina slurry sequentially and then washed ultrasonically in water and ethanol for a few minutes, respectively. A small quantity of the CNTs-IL gel was immobilized on the GCE surface and smoothed on a weighing paper to get an even film covering the electrode surface (noted as CNTs-IL/GCE). 6 μL BOD (1 mg/L) was dropped on the CNTs-IL/GCE surface and dried at 4 °C for 12 hours (noted as BOD/CNTs-IL/GCE). The BOD/GCE was prepared with the same procedures on GCE.

Instrumentation. Electrochemical SEM images were taken with a XL30 field-emission scanning electron microscope at an accelerating voltage of 15 kV. XRD patterns were collected by a D8 ADVANCE (Germany) with Cu Kα radiation (λ=1.54056 Å) in the range of 20-80º (2θ). Photoelectrochemical (PEC) studies were carried out in a conventional three electrode system with a platinum foil as the counter electrode and Ag/AgCl (saturated KCl) as the reference electrode. Light-driven biofuel cell (LBFC) studied were performed using a two electrode system with a TNTs photoanode and a BOD/CNTs-IL/GC biocathode. All electrochemical measurements were recorded by a CHI 832C electrochemical workstation (Chenhua Co., Shanghai). UV lamp (GE, Japan G4T5) with central wavelength 365 nm was chosen as a UV light source. Three LBFC systems including TNTs photoanode and BOD/CNTs-IL/carbon cloth biocathode in series were installed under UV light

illumination to light a LED.

Figure

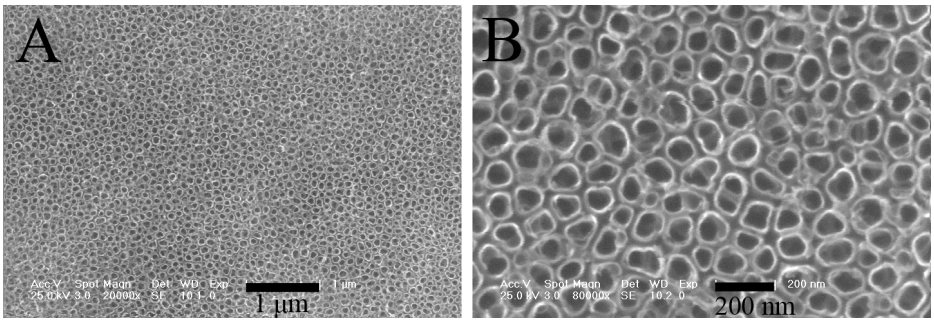

Fig. S1. The typical SEM images of TiO_2 nanotubes with different magnifications.

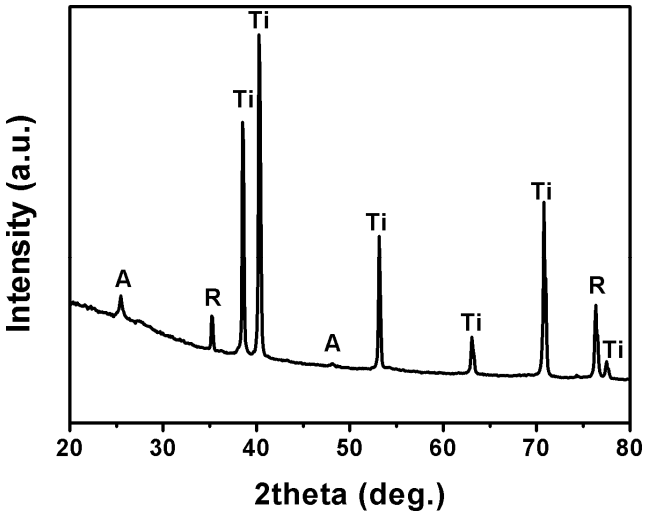

Fig. S2. The typical XRD pattern of the TiO_2 Nanotubes electrode.

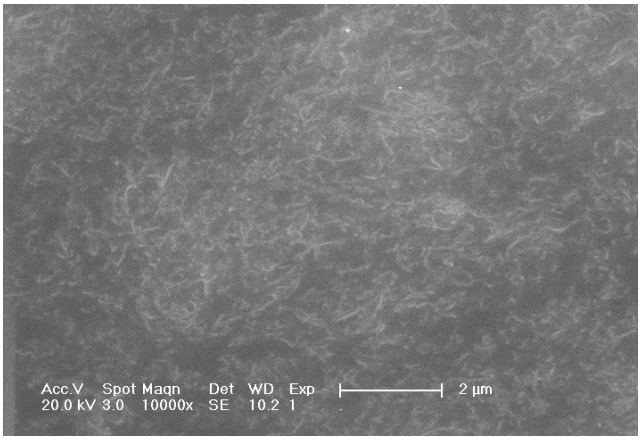

Fig. S3. The typical SEM image of CNTs-IL nanocomposites.

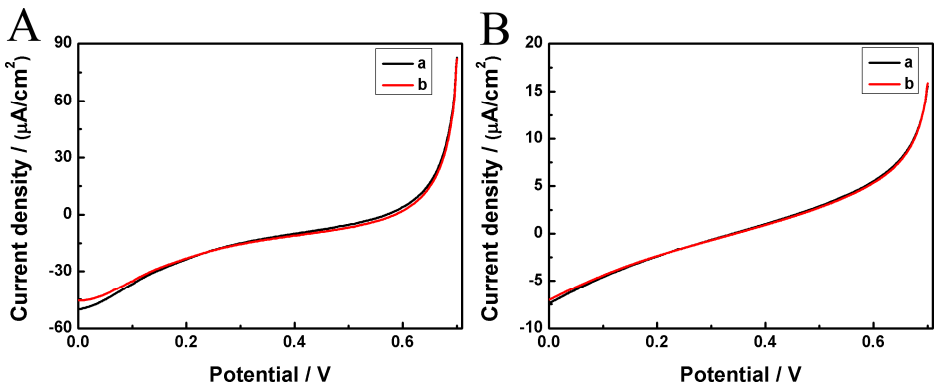

Fig. S4. Linear sweep voltammagrams of CNTs-IL/GCE (A) and BOD/ GCE (B) in (a) air saturated and (b) N_2 saturated PBS (pH 7.0).

Reference

1. Z. Liu, X. Zhang, S. Nishimoto, M. Jin, D. A. Tryk, T. Murakami, A. Fujishima, Highly Ordered TiO_2 Nanotube Arrays with Controllable Length for Photoelectrocatalytic Degradation of Phenol, *J. Phys. Chem. C* 2008, **112**, 253-259.