Electronic Supplementary Information (ESI):

Macroporous monolithic Magnéli-phase titanium suboxides anode for effective bioelectricity generation in microbial fuel cells

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Preparation of macroporous monolithic titanium suboxides (MM-TiSO) electrode

The MM-TiSO was prepared by high-temperature H_2 reduction of TiO_2. In brief, the rutile TiO_2 powders were mixed by water and isopropanol (1:1, v/v) to decrease the capillary force of powder, followed by reduction at H_2 atmosphere at 1050 °C for 4 h. The as-prepared Ti_4O_7 powders were cleaned, dried, and added 5% (w/w) polyethylene oxide solution binder and carbon as porosity-producing agent, and then the mixture was compressed in a uniaxial press at 20 MPa to form a plate shape with diameter size of 3 cm. The plate blocks were sintered in air to remove the impurities.

Characterizations

The X−ray diffraction (XRD) analysis was conducted with an X−ray diffractometer (Bruke D8 Adv., Germany) using Cu K α radiation (λ = 0.15406 nm) at a power of 40 keV3×30 mA. The chemical compositions of the materials were identified by using an X−ray photoelectron spectrometer (XPS;

PH1-5700 ESCA system, U.S.) equipped with a hemispherical analyzer and an aluminum anode (monochromatic Al Kα 1486.6 eV) as source (at 12−14 KV and 10−20 mA). The morphology of the electrode and biofilm was observed by using field−emission scanning electron microscopy (SEM, Helios Nanolab600i, FEI, U.S.).

The electrochemical behaviors of MM-TiSO monolith were investigated using three–electrode cell based on PARSTAT (CHI700D, Chenhua Co. Ltd., China) electrochemical system at room temperature (25 °C). The bioelectrochemical properties were examined using a small glass cylinder (5.0 mL) mounted with a silicone elastomer cap as the electrochemical cell, and all the experiments were done at scan rate of 1mV s^{-1} unless stated otherwise. The transfer coefficient (α) and heterogeneous electron transfer rate constant (k_s) were estimated by Loviron's theory.[50] Current density and power density normalized to the cathode surface area (A cm^2 and W m^{-2}) were calculated from $j=I/A$ and $P=IU/A$. Electrochemical impedance spectroscopy (EIS) was conducted over the frequency range of 100000 Hz to 0.01 Hz with a sinusoidal perturbation of 10 mV. Tafel plots were recorded for each anode by sweeping voltage from η = 0±80 mV at 1 mV s^{-1}, where η = 0 is the open circuit potential (OCP) of the anode versus the reference electrode (SCE).

MFC construction and operation

The anode of MFC reactors was inoculated with mixed cultured well-running reactor in the Lab., and the media contained acetate (0.82 g L^{-1}), NH_4Cl (0.31 g L^{-1}), $NaH_2PO_4{\cdot}2H_2O$ (3.321 g L^{-1}), $Na_2HPO_4{\cdot}12H_2O$ (10.3174 g L^{-1}), KCl (0.13 g L^{-1}), trace minerals (12.5 mL L^{-1}), and vitamins (5 mL L^{-1}). Reactors were operated in fed-batch mode at 30±1 °C, and substrates were replaced when voltage is lower than 50 mV. The cell voltage data was collected by using an on–line data acquisition system (Model 2700, Keithley Instruments, Inc., Cleveland, OH, U.S.), and then converted to power density. Cubic-shaped single-chamber MFC reactor (28 mL, 4 cm long cylindrical chamber) was made up with different anodes placed on the opposite side of Plexiglas tube at a fixed external circuit resistance of 1000 Ω. All tests were conducted at least three duplicates, with average values (±S.D.) of duplicates given in the text. Only one of these duplicates was shown in the figures for clarity.

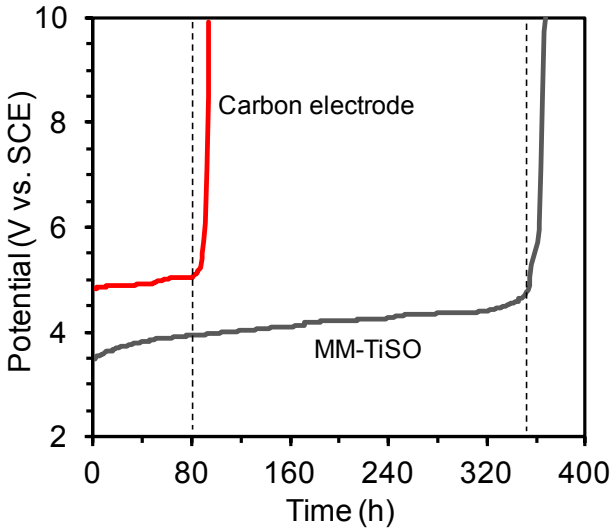

Fig. S1 Time course of potential during accelerated life tests in 3.0 mol L^{-1} H_2SO_4 at current density of 1.0 A cm^{-2} and temperature of 30 °C.[52]

Table S1 Comparison of MFC performances for different anode materials.

Anode	Morphology	Electrolyte (PBS, mM)	OCV (V)	Power density (mW m^{-2})	Ref.
Graphene	Monolithic	50	0.623	897.1	[39]
CNT hydrogel	Porous	50	0.566	132	[40]
Polypyrrole	Nanotube	50	0.593	612	[41]
MnO_2 framework	Macroporous	50	0.695	596.5	[42]
CP/GNRs/PANI	Nanowire	100	0.785	856	[43]