CNFs @ MnO_2 nanofiber as anode for improving extracellular electron transfer of microbial fuel cells

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SI. Characterization and methodology

1.1Material characterization

The surface morphology and structural characteristics of the prepared materials were analyzed by field emission scanning electron microscopy (FESEM, SUPRA 55). The crystal structure of the samples has been obtained in the 2θ range between 20° and 80° using X-ray diffraction (XRD) and 3,320 TTR in Japan. Raman, LabRAM HR Evolution, HoRIBA JobinYvon, France, was used to study the degree of graphitization of the material using a He-Ne laser with a wavelength of 532 nm. Brunauer-Emmett-Telle (r BET) and Barrett-Joyner-Halenda (BJH) methods were used respectively (TriStar II 3Flex, Micromeritics, The N2 adsorption-desorption curves and pore size distribution of the samples were determined. X-ray photoelectron spectroscopy (XPS, ULVAC-PHI.INC., Japan) measurements were performed on PHI5000 Versaprobe (ULVAC-PHI.INC., Japan) to determine the surface chemical state of the material. After the MFC run, protein concentrations on different anodes were measured using the Bradford protein quantification kit. Morphology and structure of biofilms were observed by FESEM and confocal laser scanning microscopy (CLSM, LSM800, Germany). The species and abundance of biofilms on anodes were measured using 16s rRNA (Majorbio, China).

1.2 MFCs construction and operation

The dual-chamber MFCs (Figure S1) with an effective working volume of 118 mL per chamber separated by a proton exchange membrane (PEM, Nafion 117, Dupont, USA) were used during the whole experiment. The prepared materials and pure CC were used as anode and cathode, respectively. The anode chamber was equipped with anode and inoculated with bacteria (anaerobic tank, Origin Water, Beijing) and anolyte. The anolyte was composed of 1 g CH_3COONa, 0.31 g NH_4Cl, 0.13 g KCl, 2.75 g NaH_2PO_4•$2H_2O$, 11.466 g Na_2HPO_4•$12H_2O$, 1 mL vitamin, and 1 mL mineral solutions. The catholyte consisted of 100 mM potassium ferricyanide. The data acquisition system (MPS-010602, China) was employed to obtain the cell voltage data points. All MFCs were operated under batch modes at 30 ℃ with an external resistance of 1000 Ω. The power density and polarization curves were obtained by changing the external resistance from 5 kΩ to 100 Ω at the steady state of MFCs. Under each resistance, the MFCs devices were kept for 20 min to ensure the output voltage stability. When the cell voltage dropped to a level below 0.05 V, both the anolyte and catholyte were replaced with fresh solutions. The chemical oxygen demand (COD) removal rate and coulombic efficiency (CE) analysis were performed to explore the pollutant removal and electron recovery capacity of the anode.

1.3 Determination of CODcr

(1) Digestion

First, 2 mL of the inlet or outlet water sample of MFC was placed in the digestion tube, then 3 mL of the digestion solution and 0.08 g of mercury sulfate were added and shaken thoroughly. The tubes were then put into the digestion apparatus and digested at 150℃ for 2 h.

(2) CODcr was measured by spectrophotometry

Firstly, standard solutions with CODcr of 0, 400, 800, 1200, 1600 and 2000 mg•L-1 were configured. These standard solutions were dissolved according to step (1), and then the absorbance value was measured at 600nm by visible ultraviolet spectrophotometer, and the standard curve was drawn. Similarly, the CODcr concentration of the water sample was tested as described above. When the concentration range is not 0-2000 mg•L-1, the standard curve for a larger COD concentration range needs to be redrawn.

1.4 Electrochemical analysis

In this study, electrochemical workstation (CHI660, China) was used to characterize the battery performance. The three-electrode system consists of working electrode, reference electrode (saturated calomel electrode) and opposite electrode (platinum sheet). CV test conditions are -600-600mV, sweep speed 10 mV•s-1; Electrochemical impedance spectroscopy (EIS) was used to analyze and

evaluate the anode material and battery performance. The EIS were measured with a disturbance amplitude of 5 mV in the frequency range of 1000 KHz-0.1Hz. The Nyquist curve obtained was fitted by circuit fitting software (ZSimpWin 3.60). The electrolyte for electrochemical measurement is anodic liquid.

1.5 Efficacy test

(1) Power density and polarization curve

When the MFC circuit voltage reaches the maximum value and remains stable, record the voltage value. The voltage is the open-circuit voltage of the battery. Then the variable resistance box is set with different external resistances (5000-100Ω), and the value of the rheostat is adjusted in the order from high to low. The output voltage at both ends of the external resistance of the MFC is measured with a multimeter, and the current corresponding to the output voltage is calculated according to Ohm's law (I=U/R). The corresponding calculation formula is as follows:

$$\text{Current density} = U/RA \quad (3\text{-}1)$$

$$\text{Power density} = IU = U^2/RA \quad (3\text{-}2)$$

U ——voltage at both ends of the circuit，V；

R ——external resistance，Ω；

I ——current，A；

A ——anode electrode area，cm^2

(2) CE

Coulomb efficiency (CE) is defined as the ratio of the generated charge to the maximum theoretical charge achievable (eq 3-3). It is a key parameter used to evaluate the performance of MFC systems. The calculation formula of CE is as follows:

$$CE = \frac{\int_0^t Idt \times M}{(COD_0 - COD_t) \times V \times F \times n} \times 100\% \quad (3\text{-}3)$$

Where, M -- molecular weight of oxygen, 32 $g \cdot mol^{-}$;

I -- current, mA;

F -- Faraday's constant, 96485 $C \cdot mol^{-1}$;

COD0 -- COD concentration of influent, $mg \cdot L^{-1}$;

CODt -- COD content of effluent, $mg \cdot L^{-1}$;

n -- the number of electrons exchanged per mole of oxygen, n=4;

V -- Volume of anode chamber, 118 mL

(3) Protein content

(I) protein standard curve drawing: protein standard curve was determined by spectrophotometer method 0, 500, 1000, 2000, 5000 $\mu g \cdot mL^{-1}$protein standard solution. The absorbance at 595 nm was measured by spectrophotometer.

(ii) Determination of water samples: The same as the standard curve determination method, the anode electrode area of 1 cm^2 was taken out, 2 mL of protein standard diluent was added, and then 3 mL of G250 staining solution was added, and the staining was performed at room temperature.

(III) Determination of absorbance at 595 nm wavelength and finally calculation of protein content based on the standard curve.

(4) Biological SEM analysis of anode electrode

SEM was used to observe the microbial distribution on the anode biofilm after bacteria enrichment. The preparation method of SEM samples was as follows: biofilm samples were placed into 5 mL centrifuge tube with tweezers, 5 ml2.5%glutaraldehyde was added, fixed at 4 ℃ for 12 h, and then washed with ethanol solution three times