Electronic Supplementary Information

Light-activated g-C_3N_4 photoelectrodes with selective molecular sieve for in vivo quantification of oxygen levels in living mouse brain

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Content

1. Reagents and Chemicals

Urea, acetone, ethanol, iodine, ascorbic acid, uric acid, NADH, $CaCl_2$, copper chloride, $FeCl_3$, $K_3[Fe(CN)_6]$ and triphenyl tetrazolium chloride (TTC) were purchased from Aladdin Chemistry Co. Multimode optical fiber (100 μm diameter) was purchased from Shanghai Fuxiang Optical Co. (China). Indium tin oxide targets were purchased from Fuzhou Infixon Optoelectronics Technology Company (China). Polysulfone (PSF) and molecular sieve ZIF-8 were purchased from Beijing Royaltech Co., Ltd. (China) Artificial cerebrospinal fluid (aCSF) was prepared by mixing NaCl (126 mM), KCl (2.4 mM), KH_2PO_4 (0.5 mM), $MgCl_2$ (0.85 mM), $CaCl_2$ (1.1 mM), $NaHCO_3$ (27.5 mM), and Na_2SO_4 (0.5 mM) into Milli-Q water, and the pH was adjusted to 7.4. H_2O_2 was purchased from GeneralReagents Co. Double-distilled water obtained from a Millipore water purification system was used in all experiments and were at room temperature. In the selectivity test, the concentrations of all interferents mentioned were selected referring to their practical amounts as reported previously.[S1- S6] All aqueous solutions were prepared by Milli-Q water (18.2 M Ω cm, Millipore).

2. Apparatus and Instruments.

The concentration of O_2 in solution was measured by Dissolved Oxygen Meters (JENCO 9173 DO). The SEM image and eds mapping were taken by scanning electron microscope (JSM-5610LV, NORAN-VANTAGE). Electrochemical experiment was performed on an electrochemical work station (CHI660D, Chenhua in Shanghai, China).

3. Preparation of photoelectrodes

A multimode fiber with an outer diameter of 100 μm was prepared as a drawn cone fiber by a laser drawing machine. Subsequently, an indium tin oxide (ITO) layer, called FO, was uniformly modified on the surface of the fiber by magnetron sputtering at a current of 300 mA for 3 min. g-C_3N_4 was electrodeposited on the surface of the fiber. g-C_3N_4 was synthesized by high-temperature thermal condensation using a nitrogen-rich small molecule, urea, as a precursor for the synthesis of g-C3N4, in a muffle furnace. The synthesized g-C_3N_4 was heated in a muffle furnace at 550 ^oC for 3 h at a rate of 5 ^oC/min, after which the g-C_3N_4 was loaded onto FO by electrophoretic deposition. Before electrophoretic deposition, the FO was washed with acetone, ethanol and deionized water for 20 min, and the deposition solution was acetone containing 0.4 g/mL I and 0.4 g/m g-C_3N_4, and sonication was required for 1 h prior to the deposition to make the g-C_3N_4 more uniformly dispersed. The g-C_3N_4-modified FO electrode, called FOC, was deposited by applying a voltage of 5 V for 1 min under a constant potentiated using FO as the cathode and a Pt electrode as the anode. The obtained FOC electrode was burned in a tube furnace by passing N_2 through it at 450 ^oC for 1 h, and then slowly cooled down to room temperature. ZIF-8@ PSF was prepared as follows: first, the PSF material was vacuum dried at 120 °C for 24 hours. Then, PSF (0.4 g) was dissolved in chloroform (3.6 g) with the addition of ZIF-8 (10% w/w). After the resulting mixture was stirred overnight, ultrasound was performed three times for one hour each time, resulting in the ZIF-8@PSF membrane solution. The ZIF-8@PSF membrane solution was spin-coated on the FOC surface to prepare FOM.

4. Electrochemical experiments

AC impedance Nernquist plots were performed in a solution containing 1 mM $K_3[Fe(CN)_6]$. Mott-Schottky curve tests were performed in 50 mM Na_2SO_4 solution. The photoelectrochemical test was initiated by a laser connected at the end of the fiber after the start-up current signal is acquired. The laser wavelength is 405 nm.

5. Mouse middle cerebral artery embolization (MCAO) animal experiments.

The animal model protocol was approved by the Animal Care and Use Committee of East China Normal University. Male C57 mice (25-30 g) were purchased from the Animal Center of East China Normal University. These mice were housed in a climate-controlled chamber with free access to food and water during a 12-hour light-dark cycle. The gas isoflurane was used for experimental animal anesthesia. Intraluminal monofilament conduction of MCAO was used and reperfusion surgery was performed. The middle cerebral artery was occluded via the internal carotid artery (ICA). First, the pterygopalatine artery of the ICA was identified and occluded with an arterial clamp. Then, a small incision was made in the right external carotid artery (ECA), and a monofilament suture was inserted into the ECA approximately 10 mm from its bifurcation. In this procedure, the right common carotid artery was occluded and perfused with the ICA pterygopalatine artery at the end of the procedure. The body temperature of the animals was maintained at 37°C during and after surgery using an insulating pad (TC-1000, Manpower Biotechnology Co., Ltd., Shanghai, China). Occlusion and reperfusion were detected using Doppler laser flowmetry (Periflux 5010, Perimed, Stockholm, Sweden). Microelectrodes were implanted into the CA1 area of the hippocampus using standard stereotactic procedures (left= 1.0 mm, posterior= -1.0 mm, depth= 2 mm).

6. SEM and EDX mapping analysis for ITO-coated fiber.

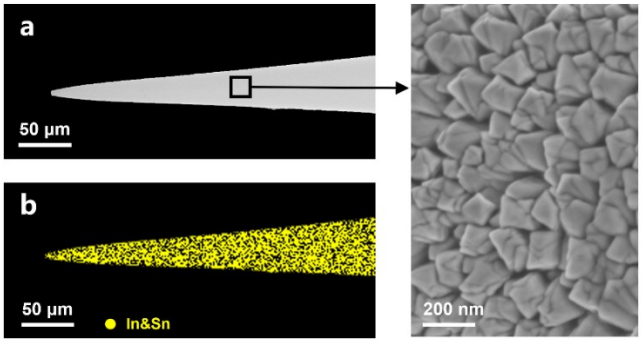

Fig. S1 SEM and EDX mapping analysis of In+Sn (yellow) for ITO-coated fiber.

7. XPS curve of FOM

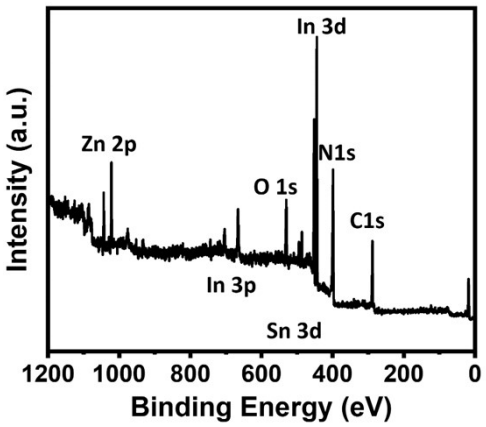

Fig. S2 XPS curve obtained at FOM.

8. Ultraviolet absorption spectra of FO, FOC and FOM.

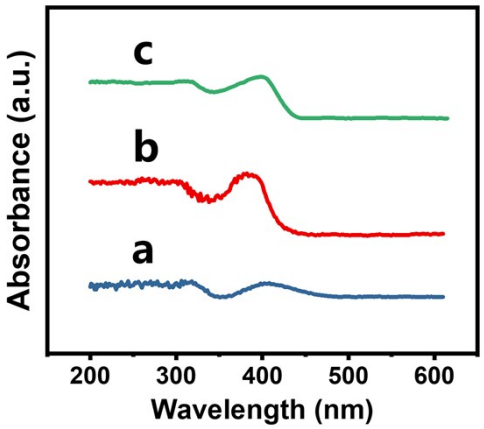

Fig. S3 UV absorption spectra of FO (a), FOC (b) and FOM (c).

9. Electrochemical impedance spectroscopy

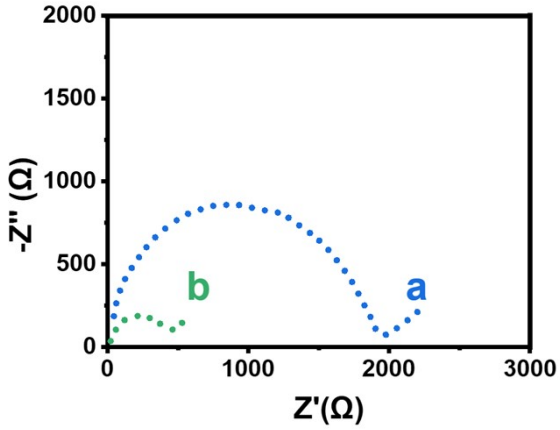

Fig. S4 Nyquist plots of FOC (a) and FOM (b) collected at open-circuit potential in 0.1 M KCl solutions.

10. N_2 adsorption-desorption isotherms of PSF@ZIF-8

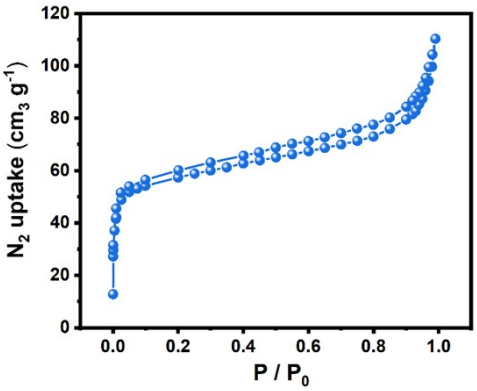

Fig. S5 N_2 adsorption-desorption isotherms of PSF@ZIF-8.

11. Comparison of detection and analysis performance of O_2

Table S1: Comparison of detection and analysis performance of O_2.

Methods	Linear range	Detection limit	Applications	Applied voltage (vs. Ag/AgCl)	Ref.
Fast-scan cyclic voltammetry by carbon fiber microelectrodes	NM	NM	In rat brain	-1.40 to 0.80 V	R1
Pt microelectrode arrays	0 μM-1.25 mM	5 μM	In rat brain	-0.50 to 0.30 V	R2
Ceramic-based multisite Pt microelectrode arrays	0-25 μM	0.33 μM	In rat brain	−0.60 V	R3
Hemin-Fc modified carbon fiber electrode	1.3-200.6 μM	NM	In mouse brain	−0.70 to 0.50 V	R4
ZIF-8@PSF g-C_3N_4 modified photoelectrode	21.6-182.1 μM	1.4 μM	In mouse brain	Without applied voltage	The present work

NM is not mentioned

12. Comparison of the performance of sensors with and without the inner reference

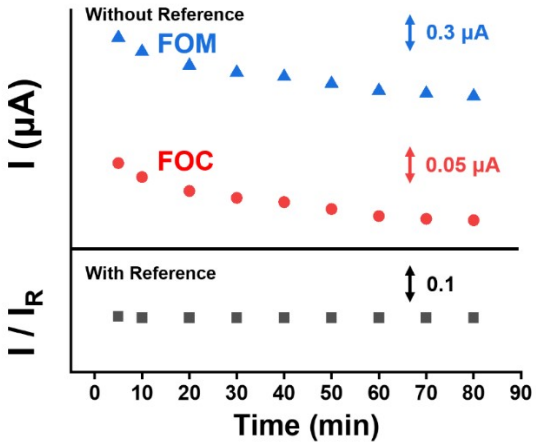

Fig. S6 Comparison of the performance of sensors with and without the inner reference in brain tissue homogenates. Upper: I value of FOC and FOM at different times. Bottom: I/I_R at different times.

13. Biocompatibility of the FOM electrode in the mouse brain.

Fig. S7 TTC-stained brain tissues obtained after implanting the FOM electrode in the mouse brain for 24 h.

14. The stability of photoelectrodes for in vivo assays

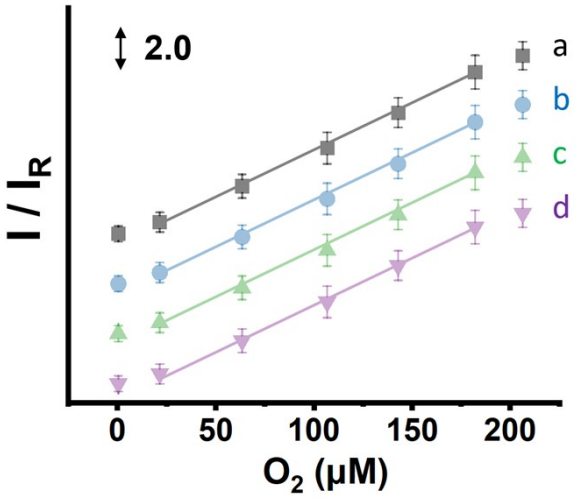

Fig. S8 Calibration curve (a) obtained at FOM in aCSF solution containing different O_2 concentrations, and the post-calibration curves after the FOM electrode was implanting in mouse brain for 6 h (b), 12 h (c), 24 h (d), respectively. Data are presented as mean ± SD (95% CI, n = 6). CI means confidence interval.

References

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