

Supporting Information

Freestanding redox buckypaper electrodes from multi-wall carbon nanotubes for bioelectrocatalytic oxygen reduction via mediated electron transfer

Mariam Bourourou,^{a,c} Kamal Elouarzaki,^a Michael Holzinger,^a Charles Agnès,^a Alan Le Goff,^a Nadège Reverdy-Bruas,^b Didier Chaussy,^b Mikael Party,^b Abderrazak Maaref^c and Serge Cosnier^{a*}

^a Département de Chimie Moléculaire (DCM), UMR-5250, CNRS-UJF 570 rue de la Chimie, BP 53, 38041 Grenoble, France. E-mail: serge.cosnier@ujf-grenoble.fr

^b LGP2 (Laboratory of Pulp and Paper Science and Graphic Arts) Grenoble INP-Pagora/CNRS UMR 5518, 461 rue de la Papeterie, CS 10065, 38402 Saint-Martin-D'hères Cedex.

^c Laboratoire des Interfaces et des Matériaux Avancés (LIMA) Faculté des sciences de Monastir Rue Salem BCHIR B.P N 56 5000 Monastir Tunisie.

Experimental Section

Methods, materials, instruments:

Laccase (120 U_{mg}⁻¹) from *Trametes versicolor*, pyrenemethylammonium hydrochloride and 2,2'-Azino-bis(3-ethylbenzothiazoline-6-sulfonic acid) potassium salt are purchased from Aldrich and stored at 4°C. Commercial-grade thin multi-walled carbon nanotubes (MWCNTs,

9.5 nm diameter, purity >95%), obtained from Nanocyl, were used as received without any purification step.

¹H-NMR spectra were recorded on a Bruker AVANCE 400 operating at 400.0 MHz. ESI mass spectra were recorded with a Bruker APEX-Qe ESI FT-ICR mass spectrometer. All electrochemical experiments were performed in an electrochemical cell with a conventional three-electrode configuration by using an Autolab pgstat100 potentiostat. The BP films were studied as working electrode with a geometric surface of 1 cm². A platinum wire was used as counter-electrode and a saturated calomel electrode (SCE) served as reference. Electrochemical measurements were performed using 0.1 molL⁻¹ phosphate buffer as electrolyte in aqueous media at room temperature. The solutions were deoxygenated by purging with argon prior to each experiment. For the performance measurements of the biocathode the solutions were re-oxygenated with a constant oxygen flow during the whole experiment.

FE-SEM images were recorded using ULTRA 55 FESEM based on the GEMINI FESEM based on the GEMINI FESEM column with beam booster (Nanotechnology Systems Division, Carl Zeiss NTS GmbH, Germany) and tungsten gun with an accelerating voltage of 3 kV and WD of 5.4 mm. The texture properties were analyzed using advanced data processing software (ADP version 5.1, Thermo Electron Corporation). The electric resistance of the buckypaper was measured by a standard programmable DC voltage/current four-point probe method using a Jandel, Universal probe connected to a current generator (Jandel, RM3).

Synthesis:

2,2'-Azino-bis(3-ethylbenzothiazoline-6-sulfonic acid) potassium salt was obtained from 2,2'-Azino-bis(3-ethylbenzothiazoline-6-sulfonic acid) diammonium salt by treatment with potassium tert-butyloxide in methanol. Azino-*bis*(3-ethylbenzothiazoline-6-sulfonic acid)

diammonium salt (500 mg, 0.91 mmol) was added to a solution of potassium *tert*-butoxide (204 mg, 1.82 mmol) in methanol (50 mL). After 30 min, the resulting suspension was filtered and yielded a white powder of 2,2'-Azino-bis(3-ethylbenzothiazoline-6-sulfonic acid) potassium salt (490 mg). Pyrenemethylamine was obtained from pyrenemethylammonium hydrochloride by extraction with dichloromethane from an aqueous NaOH solution: pyrenemethylammonium hydrochloride (268 mg, 1.0 mmol) was added to a solution of NaOH (60 mg, 1.5 mmol) in water (30 mL). The resulting suspension was extracted with CH₂Cl₂ (3×20 mL). Removal of the solvent under vacuum yields a white powder of pyrenemethylamine (205 mg, 0.9 mmol, 90%). 2,2'-Azino-bis(3-ethylbenzothiazoline-6-sulfonic acid) potassium salt (300 mg, 0.51 mmol), BOP Benzotriazol-1-yloxy-tris(dimethylamino)phosphoniumhexafluorophosphate (272 mg, 1.02 mmol) and pyrenemethylamine (451 mg, 1.02 mmol) were dissolved in dichloromethane, CH₂Cl₂ (20 mL) and an excess of triethylamine was added. The resulting suspension was stirred at room temperature for 24 h under argon atmosphere. The reaction mixture was filtered off and the precipitated solid was washed successively with 0.1 M NaOH, dichloromethane and CF₃COOH (pH 3). Finally, the pure product was obtained as a greenish white solid (250 mg, 65 %).

¹H NMR (DMSO-d₆, 300 MHz): δ (ppm) = 1.30 (6H, t), 4.03 (4H, q), 4.84 (4H, s), 7-7.8 (6H, d), 7.8-8.6 (18H, m).

¹³C NMR (DMSO-d₆, 300 MHz): δ (ppm) = 11.46, 38.5, 40.0, 107.7, 119.8, 122.5, 122.8, 123.5, 123.5, 124.0, 125.4, 124.7, 125.6, 126.5, 127.1, 127.3, 127.7, 127.8, 128.0, 128.5, 130.0, 130.6, 131.0, 124.7, 140.2, 141.2, 157.1 .