

Designing Hybrid Nanotubes Wires for Highly Efficient Bioelectrochemical Devices

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Abstract

Introduction

Poor electron transfer and slow mass transport of substrate are significant rate-limiting steps in electrochemical systems. It is especially true in biological media where the concentrations and diffusion coefficients of substrates are low, hindering development of power systems for miniaturized biomedical devices. Here we show that the newly engineered porous microwires comprised of assembled and oriented carbon nanotubes (CNT) overcome both the limitations of small dimensions and large specific surface area. Their improved performances are demonstrated by comparing the electroreduction of oxygen to water in saline buffer on carbon and CNT fibers. Under air, and after several hours of operation, we show that CNT microwire exhibit more than ten-fold higher performances than conventional carbon fibers. Consequently, under physiological conditions, the maximum power density of a miniature membrane less glucose/O₂ CNT biofuel cell exceeds by far the power density obtained for current state of the art carbon fiber biofuel cells.

Reagents

Bilirubin oxidase (BOD) (EC 1.3.3.5) from *Trachyderma tsunodae* was purchased from Amano (Lombard, IL) and purified as described previously.⁽¹⁾ Glucose oxidase (GOx) from *Aspergillus niger* (EC 1.1.3.4, 208 U/mg) was purchased from Fluka (Sigma-Aldrich, Saint-Louis, MO) and purified as previously described.⁽²⁾ Poly(ethylene glycol)(400)diglycidyl ether (PEGDGE) was purchased from Polysciences, Inc. (Warrington, PA), poly(vinyl alcohol) (PVA, MW 195000) from Kuraray Europe GmbH (Germany) and sodium dodecyl sulphate (SDS) from Aldrich (France) and used as received. The synthesis of the BOD-wiring redox polymer PAA-PVI-[Os(4,4'-dichloro-2,2'-bipyridine)₂Cl]^{+2/+} and of the GOX-wiring polymer PVP-[Os(N,N'-alkylated-2,2'-biimidazole)₃]^{2+/3} were reported earlier.^(3,4) Single-Walled Carbon Nanotubes (CNTs) produced from a high pressure CO disproportionation (HiPco) process was purchased from Carbon Nanotech. Inc. (Houston, USA). All aqueous solutions were prepared with Millipore ultrapure water.

Equipment

The measurements were performed using a potentiostat (CH Instruments, model CHI 760C, Austin, TX, USA) and a dedicated computer. A platinum spiral wire was used as counter electrode and all potentials were referred to a Ag/AgCl (3 M KCl) electrode. Either carbon nanotube fibers (CNF) or carbon fibers (CF) were used as working electrode. The Morphology of CNT fiber and carbon fiber was characterized by Field Emission Scanning Electron Microscope (Model JSM-6700F, JEOL, Japan) operated at a voltage of 5.0 kV. The sample was prepared by fixing CNF fiber or carbon fiber on a SEM stage using carbon tape.

Procedure

****Fiber Synthesis.**** 1) Purify CNTs by acid treatment before making fibers. Typically, heat 250 mg of CNTs at 200 °C in oven for 8 h, then placed in a flask. Pour 1 L concentrated HCl (37%, v/v) into the flask and incubate for 4 h under agitation. (The color of the solution became yellow because of the dissolution of Fe³⁺ ions) 2) After suction filtration, wash the tubes several times with deionized water and lyophilize. 3) Make the CNT fibers by a particle coagulation spinning (PCS) process.(5,6) Disperse CNT in a aqueous solutions of SDS (1.0 wt %) and sonicate. 4) Inject a relatively concentrated aqueous CNT suspension (0.3 wt %) through a cylindrical syringe in the co-flowing stream of a coagulating bath containing polyvinyl alcohol (PVA) solution (5 %, wt %). As a result, the CNTs aggregate and form gel like fibers. 5) Wash the gel fibers several times with pure water in order to remove most of the surfactant and some fraction of PVA. 6) Pull out the fibers out of water and dry. 7) Heat the fibers at a temperature of 600 °C for 2 h under argon atmosphere to completely remove the PVA. ****Electrodes preparation.**** Make the CNF electrode as follows: 1) Place a single fiber in a 1-mm polycarbonate groove. 2) Fix one end of the fiber with epoxy, and connect electrically the other end to a copper wire with conductive carbon paint. 3) Let the the carbon paint dry and then insulate with a layer of epoxy. 4) Prior to coating the bioelectrocatalysts, make the CNF hydrophilic by plasmas oxidation (1 Torr O₂ plasma, 20 min).

Critical Steps

1) As-produced CNT fibers consist of an interconnected network of PVA chains and CNTs. They exhibit a high toughness. But they are not suitable as such for electrochemical applications. Indeed the PVA limits the porosity of the fibers and the access to the CNT interface. This is why the fibers were heated at a temperature of 600 °C for 2 h under argon atmosphere to completely remove the PVA. After this thermal treatment, the fibers are electrically conductive and only composed of CNT without any additives or binders. They exhibit a high porosity and are therefore suitable for electrochemical applications. 2) The diameter of the fibers can be controlled by the flows in the spinning process. 3) ****Fiber properties and electrochemical characterizations.**** The carbon nanotube fibers are electrically conductive and exhibit a conductivity of 50 S.cm⁻¹ as measured by a Keythley 2000 multimeter between two silver paint connections. The CNT fiber electrochemical capacitance measured in a 1M NaCl aqueous solution is about 20F/cm³. The BET surface area was measured by nitrogen adsorption desorption experiments at 77.4K as previously reported for similar fibers.(7) It is about 300m²/g. Increasing the porosity of an electrode material is a key to increase its electroactive surface area. Nevertheless a direct determination of the actual microscopic area of a microelectrode from electrochemical measurements is not straightforward. Indeed, features of roughness smaller than the diffusion length tend to be averaged within the diffusion field.(8) This is why comparisons of electrochemical capacitance and BET surface area should be taken with some caution.

References

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