A HIGH-PERFORMANCE PHOTO-BIOSUPERCAPACITOR BASED ON MANGANESE OXIDE/CARBON NANOTUBE/PEDOT:PSS NANOCOMPOSITES

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ABSTRACT

A high energy-density supercapacitor is currently undergoing exciting development with an entirely new kind of electric power device: a biosupercapacitor in which electric energy is simultaneously acquired and stored. This new hybrid device integrates the energy harvesting function of an electrochemical energy storage device (e.g. bio-solar cells) with the high-power operation of an internal supercapacitor. Manganese oxide/carbon nanotube/poly(3,4-ethylene dioxythiophene):polystyrene sulfonate nanocomposites on carbon cloth were developed as a novel anode for the biosupercapacitor. Cyanobacterial biofilm formed on the anode provided 3-D double-functional electrode concurrently exhibiting solar-driven energy-generating and storing features, generating maximum power and current density of 25.48μW/cm^2 and 115.81μA/cm^2, respectively, which is the highest reported success of any existing biosupercapacitors. The 3-D dual-feature bioanode demonstrated superior capacitive behaviors, electrochemical properties, a high rate of bacterial extracellular electron transfer, and efficient mass transfer to and from the electrode, all of which led to high power generation.

KEYWORDS

Biosupercapacitors; self-charging supercapacitors; Supercapacitive energy harvesters; bio-solar cells;

INTRODUCTION

Recently, researchers showed that the bioanode of bio-electrochemical systems can store charges and offer bio-electrocatalytic capabilities; the two functions allow capacitive components to be internally integrated in the systems [1-7]. The capacitive anode accomplishes high power discharges after it is simultaneously recharged by the energy harvesting system. This approach, named bio-supercapacitor, is gaining acceptance as a future energy technique, especially in the field of biological fuel cells. Several studies of these hybrid devices combine supercapacitors and bio-electrochemical systems such as enzymatic fuel cells, microbial fuel cells, and photosynthetic enzymatic (or sub-cellular) fuel cells [6-10]. This concept indicates the possibility that even low-performance biological fuel cells can become a superior substitute to conventional batteries or other energy harvesting techniques. Recently, we successfully demonstrated that bio-solar cells using living photosynthetic organisms could be integrated with supercapacitors [11]. However, the full potential of the hybrid devices for high-performance energy production and power storage was not fully realized because of the low super-capacitive performance of the anode.

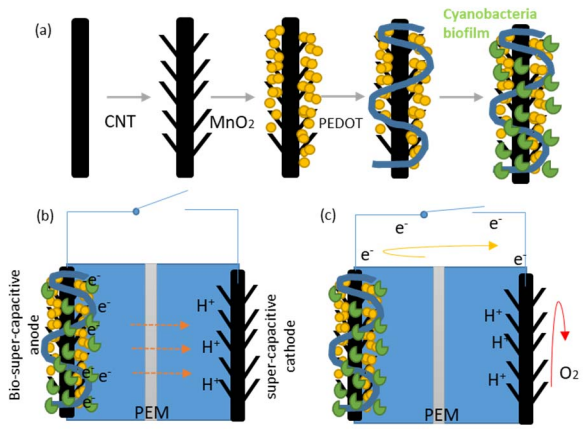

Figure 1: Schematic illustrations for (a) the preparation process of the biosupercapacitive anode. Schematic diagram of the device during (b) charging and (c) discharging.

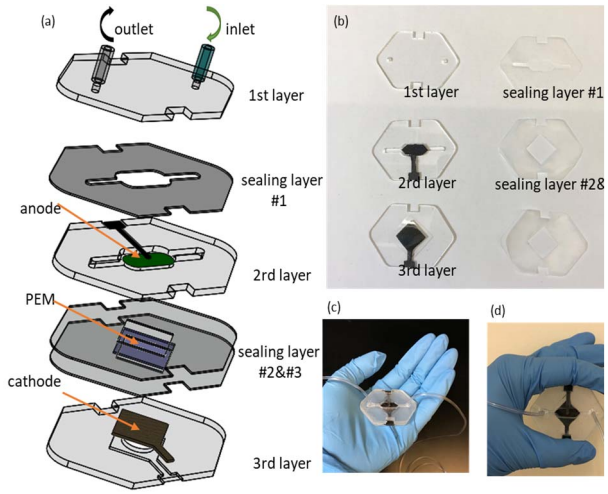

Figure 2: (a) Schematic illustration and (b)photo images of individual layers of the device. (c) & (d) Photo images of the assembled device.

In this work, we integrated up-to-date supercapacitor technologies into the bio-solar cell [12]. The overall capacitance enhancement derived from the combined contribution of the pseudocapacitance of MnO_2 and the electric double layer capacitance of CNTs, while the PEDOT:PSS polymer offered superior bacterial affinity and bioelectrocatalytic properties (Figure 1). The integration of the internal supercapacitor within the bio-solar cell was performed, where the charge-storage and energy harvesting functioned simultaneously (Figure 2). In

open circuit mode, device voltage was determined by the equilibrium potentials of the electrodes. The photo-bio-electrocatalytic and redox reaction polarized the anode/cathode toward values that were more negative and positive than the typical equilibrium potential. Excess negative and positive charges at the electrodes were balanced by counter ions from the electrolyte forming an electrochemical double layer at each electrode of the device. In this way, the hybrid device could electrostatically store charge/energy. The device could be then discharged by a rapid electrostatic process under short circuit conditions; the energy electrostatically stored was delivered with high and short discharge pulses and high-power output could be achieved.

MATERIALS AND METHODS

Bacterial Inoculum

Synechocystis sp. PCC 6803 were grown from • 80 °C glycerol stock cultures by inoculating in a 15 mL of BG-11 medium with gentle shaking under 12 hours light and dark intervals [13, 14]. The BG-11 contained 1.5 g of $NaNO_3$, 40 mg of K_2HPO_4, 75 mg of $MgSO_4$, 36 mg of $CaCl_2$, 1 mg of EDTA, and 6 mg of citric acid and of ferric ammonium citrate per 1 L of distilled water. A fluorescent lamp-controlled chamber provided continuous aeration at 30 ± 2 °C and illumination for 2 weeks. Growth was monitored by measuring the optical density at 600 nm (OD_{600}) and the culture reached an OD_{600} of 1.2.

Supercapacitive Nanocomposite Anodes

100 mg MnO_2(99% pure fine power, Loud Wolf Industrial& Scientific), 100 mg carbon nanotube (multi-walled, Sigma Aldrich), and 2mL PEDOT:PSS (1% solution, Clevious PH 1000, Heraeus) were mixed and sonicated for 1 hour, and the colloidal inks were poured to a petri-dish on a hot plate. Then further stirring process was done at 60 °C. The anode was then fabricated by airbrushing the colloidal ink on the carbon cloth. The anode was heated at 120 °C in the oven for 2 hours. Finally, the anode was put in the microwave oven for 4 minutes for improving its porosity.

Device Fabrication and Bacteria Loading

The device consisted of five functional layers: a top polymethyl methacrylate (PMMA) layer, a parafilm sealing layer #1, a PMMA reservoir layer, a proton exchange membrane (PEM, Nafion 117) layer including two parafilm gasket layers (#2 & #3), and a bottom air-cathode layer. All layers were aligned and assembled by hot-pressing. The inlet and outlet tubes enabled the initial introduction of the bacterial inoculum. Once the cyanobacteria cells were injected into the microfluidic channel, they attached to the three-dimensional anode and accumulated onto it, forming a biofilm.

Electrochemical analysis

By using the potential station (Squidstat Plus, Admiral Instruments), cyclic voltammetry (CV) was carried out to evaluate the anodes' electrochemical performance. All the CV tests were performed in a three-electrode electrochemical cell. The test cell consisted of the carbon-cloth anode and the platinum foil cathode. A commercially available Ag/AgCl (in saturated KCl) electrode was used as a reference electrode. Our supercapacitive material (CNT/MnO_2/PEDOT:PSS) was mounted on the carbon-cloth anode and their electrochemical performances were tested in 1 M Na_2SO_4 at a scan rate of 20 mV/s from -0.2V to 0.4V voltage window. The CV tests of cyanobacteria biofilm were conducted in BG-11 media at a scan rate of 20 mV/s from -0.2V to 0.4V voltage window. The biofilm was pre-cultured on the supercapacitive material for 5 days.

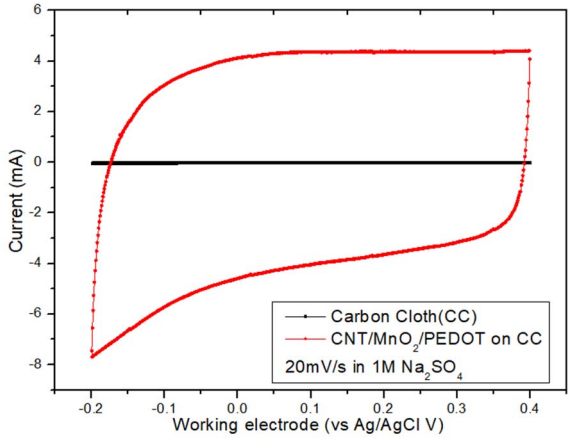

Figure 3: Comparison between CV curves of bare carbon cloth and nanocomposite deposited one

Bacterial fixation and SEM imaging

The SEM samples were treated with 4% glutaraldehyde solution (Sigma-Aldrich) overnight at 4 °C and rinsed three times with 0.1 M phosphate buffer saline (PBS). The samples were then dehydrated by 5-min serial transfers through 50, 70, 80, 90, 95, and 100% ethanol. The samples were placed in hexamethyldisilizane (HMDS) right after for 10 min and then placed in desiccator to air dry overnight. Fixed samples were examined using a FESEM (Field Emission SEM) (Supra 55 VP, Zeiss).

Electrical measurement setup

Electrical potentials between the anode and cathode were monitored by a data acquisition system (DI-720-EN, DATAQ Instruments). The polarization and power curves were measured by a customized circuit, measuring the maximum current value at various external resistive loadings. All the output values were measured after the device was fully charged. The current through a resistor was calculated using Ohm's law. Current/power density and an areal capacitance were normalized to the anode area (0.385 cm^2). All the experiments were done in the temperature/light-controllable incubator (The VWR® Signature™ Diurnal Growth Incubator, Model 2015).

RESULTS AND DISCUSSION

Electrochemical Performance of Nanocomposite Supercapacitive Material

We first investigated the electrochemical performance of the proposed CNT/MnO_2/PEDOT:PSS nanocomposite as a supercapacitor. CV results of the anodic material in 1M

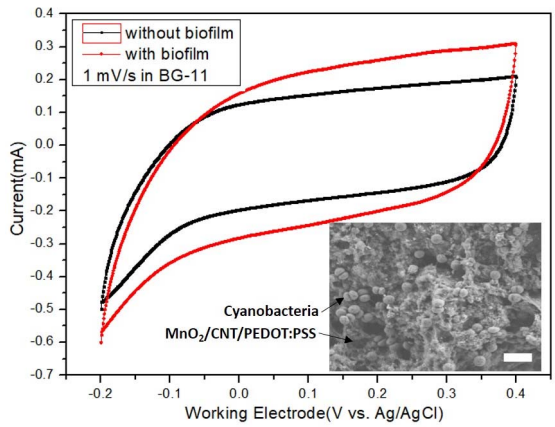

Figure 4: CV curves of the anode with or without biofilm. SEM image of the bioanode is also provided.

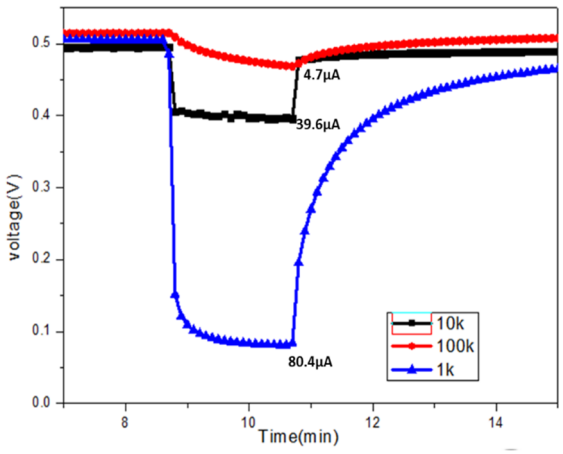

Figure 5: Discharging curves under different resistors (1 kΩ,10 kΩ and 100 kΩ)

Na_2SO_4 solution at a scan rate of 20 mV/s are depicted in Figure 3. The CNT/MnO_2/PEDOT:PSS nanocomposite on the carbon cloth shows rectangular CV shape, indicating highly reversible capacitive behavior. The capacitance was negligible without the nanocomposite, which demonstrates that redox interactions in MnO_2 and PEDOT:PSS generate pseudocapacitance while the double-layer capacitance was aroused from the CNT layer.

Electrochemical Performance of Cyanobacterial Biofilm

Evidently, more current was generated with biofilm formation on the anode. In the cyanobacterial biofilm, electrons are recovered through a water-splitting reaction and/or photosynthetic electron transport chain during light illumination, followed by the respiratory activities (Figure 4).

Charging/Discharging

The device is charged when the external electric circuit is open, and it is discharged when the circuit is closed with a given resistor (1kΩ, 10kΩ, or 100kΩ) (Figure 5). Before discharging, the device was charged for 28

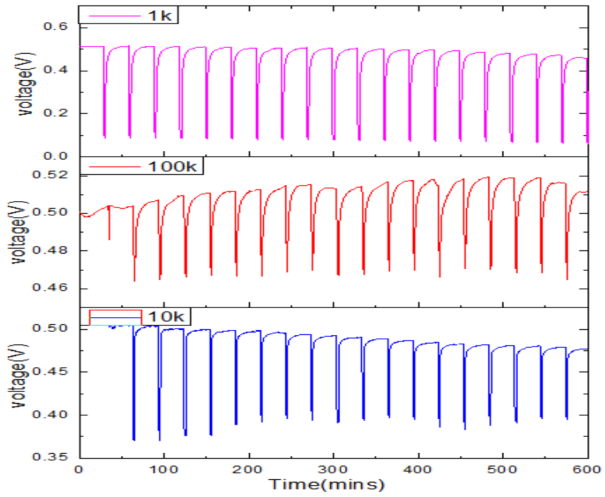

Figure 6: Charging and discharging voltage curves with different external resistors

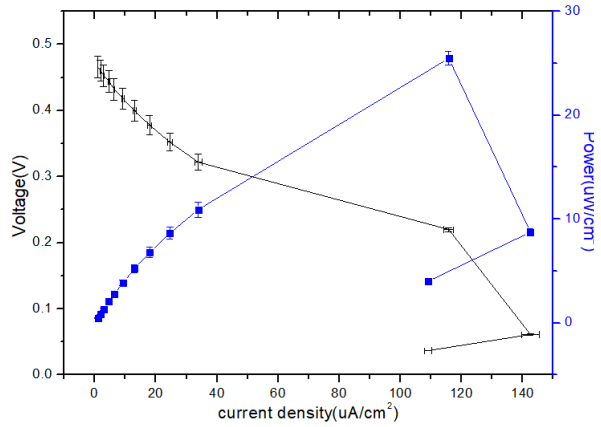

Figure 7: Polarization curve and power output of the biosupercapacitor

minutes. At 1kΩ, the output voltage decreased within several seconds and stabilized at 80mV, corresponding to 80μA. At 10kΩ and 100kΩ, the device generated 39.6μA and 4.7μA, respectively. The operational stability of the device was assessed by repeating charge-discharge cycles (Figure 6). The durability of the established voltage and thus the stability of the device at all resistances were good enough for practical applications.

Power and Current Densities

The maximum power and current density were 25.48μW/cm^2 under current density 115.81μA/cm^2, respectively (Figure 7). The supercapacitive bioanode concurrently demonstrated bio-electrocatalytic and charge-storage features which could offer the high-energy harvesting function of bio-solar cells and the high-power operation of an internal supercapacitor for charging and discharging.

CONCLUSION

In this work, we created an innovative photo-biosupercapacitor with significantly improved

supercapacitive behaviors by using MnO_2/CNT/PEDOT:PSS nanocomposites on carbon cloth. The supercapacitive nanocomposites were integrated into a well-controlled, tightly enclosed microfluidic chamber, where the charge-storage and solar energy harvesting functions worked simultaneously. This work demonstrates the possibility that even low-performance bio-solar cells can become a superior substitute to conventional batteries or other energy harvesting techniques.

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