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Advanced MnO_2/CNT ultracapacitors- Transition from planar to micropatterned array electrodes

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Ultracapacitors with substantially higher power and energy densities, faster charge/discharge capability and longer cycle lifetime have received considerable attention [1,2]. CNTs excel as EDLCs, because they are excellent electrical conductors, have very large specific surface area to volume ratio, chemically and thermally stable, and can be fabricated at lower costs than other materials [1]. However, pure CNTs have low specific capacitance, usually below 40 F/g, depending on the purity, microstructure, and type of electrolyte [3].

Pseudocapacitive transition metal oxides, which produce higher capacitance than double layer carbonaceous materials, are being studied; among which conductive RuO_2 shows outstanding performance. However, its high cost hinders it from large-scale application. Research efforts have been focused on alternative low cost transition-metal oxide MnO_2 because of its high energy density, environmental compatibility and natural abundance [1-3]. The high theoretical specific capacitance is due to pseudocapacitive behavior involving rapid, reversible faradaic reactions where the oxidation state of Mn varies between +3 and +4 in conjunction with the intercalation and deintercalation of the electrolyte cation, as represented by equation *(i)* [1,2].

$MnO_2 + K^+ + e^- \leftrightarrow MnOOK$ *(K= H, Li, Na, K)* *(i)*

However, MnO_2 shows low capacitance without conductive additives due to its intrinsically poor electrical conductivity [2,3]. One possible solution involves the use of MnO_2 with multi-walled CNTs.

In this paper, we present fabrication and characterization of ***planar and advanced micropatterned CNT/MnO_2 microelectrode array (MEA) electrodes*** by direct electrochemical deposition of MnO_2 on vertically aligned CNTs. Such an array structure provides a 3-D surface allowing for better MnO_2 incorporation as well as enhanced mobility of the electrolyte to access the interior of the porous CNT/MnO_2 microelectrodes.

A highly doped n-type silicon substrate was first oxidized to form a thin-layer of SiO_2 followed by UV photolithography step to define the array layout. The exposed SiO_2 regions were etched using BOE solution and then thin-films of the buffer layer (Ti) and the catalyst (Co) were sputtered. After photo-resist lift-off, vertically aligned multi-walled CNTs were grown using hot-filament CVD process with methane as the carbon gas source. The height of the CNTs was controlled by varying the duration of CH_4 gas flow. This process can be adapted to fabricate arrays with different geometries and dimensions. The SEM images in figures 1(a) and (b) shows the planar MnO_2 coated CNTs and the porous MnO_2 microstructure. Before and after MnO_2 deposition SEM micrographs for the microelectrode array can be seen in figures 2(a) and (b), respectively.

Electrochemical characterization of the novel ultracapacitors was performed in a flat cell using cyclic voltammetry in a 3 electrode configuration with 0.1M KCl as the supporting electrolyte. Platinum coil was used as the counter electrode with a Ag/AgCl reference electrode. The cyclic voltammograms recorded at 50mV/s, before and after MnO_2 deposition, can be seen for the planar and the MEA electrodes in figures 1(c) and 2(c) respectively. The **planar electrode** delivers a maximum capacitance of 50mF/cm^2 or **30F/cm^3** which represents a **10-fold** enhancement due to MnO_2 incorporation. In contrast, the **MnO_2/CNT MEA** delivers a maximum capacitance of 1.8F/cm^2 or **240F/cm^3**, more than **200-fold** enhancement due to MnO_2 pseudocapacitance. These results highlight the advantages of using the advanced 3-D nanostructured MnO_2/CNT microelectrode arrays.

Fabrication and characterization of the CNT/MnO_2 planar and MEA ultracapacitors will be presented.

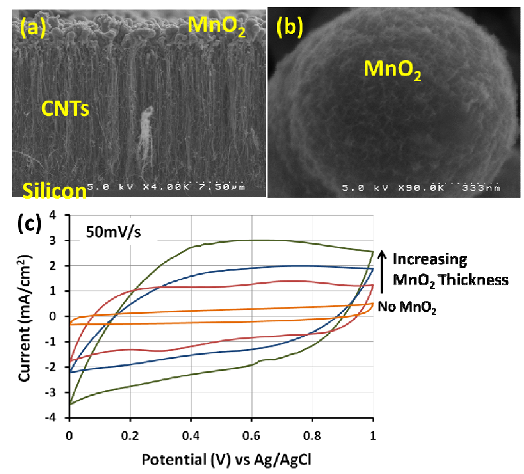

Figure 1.(a)Cross-section SEM of MnO_2 coated CNT planar electrode; (b)High resolution image of porous MnO_2; CVs recorded at 50mV/s showing enhancement in capacitance with addition of MnO_2 on CNTs.

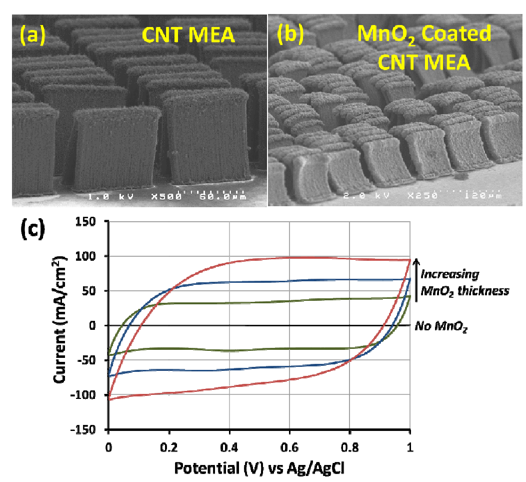

Figure 2. (a)Tilt-view- SEM micrograph of the CNT MEA; (b) Tilt-view- SEM micrograph of the MnO_2 coated CNT MEA; (c) CVs recorded at 50mV/s showing enhancement in capacitance with addition of MnO_2 on CNTs, much greater than the planar ultracapacitor electrode.

References:

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