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DRIE Si Nanowire Arrays Supported Nano-Carbon Film for Deriving High Specific Energy Supercapacitors On-Chip

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Abstract. Supercapacitor is a promising solution to storage of pulsed energy generated by MEMS energy harvesting systems, relying on its faster charging/discharging capability than secondary battery. To improve the energy density of on-chip supercapacitor which shows potential for integration with MEMS devices, in this paper we first present a successful electrode design for high specific energy pseudo-supercapacitors on the basis of deep reactive ion etched Si nanowire array supported nano-carbon matrix. Widely used pseudo-capacitive manganese oxide active material is facilely deposited into the conductive nano-carbon matrix by a chemical bath deposition. The derived electrode exhibits a remarkable capacitance increase (around 4.5x enhancement) compared with the nano-carbon matrix benefiting from the contribution of pseudo-capacitive manganese oxide. Assembled sandwich prototype on-chip supercapacitors with a symmetric configuration offer a high specific capacitance of 741.6 mF cm^{-2} when discharged at 1 mA cm^{-2}, and the energy density can attain as high as 51.5 μWh cm^{-2}. The achieved high specific energy makes such on-chip supercapacitors attractive in the field of energy collection when cooperated with micro- or nano- energy generators.

1. Introduction

On-chip supercapacitors have been widely investigated due to their potentials in integral application with other MEMS devices (e.g, energy harvesting systems, sensors) to realize self-powered system, which is meaningful for intensively pursued Internet of Things [1]. Moreover, on-chip supercapacitors are more suitable for use than secondary batteries, especially regarding the synergistic combination with high frequency energy harvesting systems which normally acquire the pulsed energy from environment and hence require the fast response for energy storage [2]. However, one main problem impeding the supercapacitor advancement is its low energy density [3]. This indicates that a larger footprint or volume for accommodating the supercapacitor part is imposed in the whole system.

In our previous study, it has been revealed that the silicon nanowire arrays (Si NWAs) fabricated by deep reactive ion etching (DRIE) can regulate the compact integration of fullerene-like carbon decorated carbon nanotubes (FC-CNTs), which led to the formation a hierarchical porous nano-carbon film with abundant macropores and mesopores yet good electric conductivity [4]. Herein, we

demonstrate an electrode design towards enhanced specific capacitance based on this porous matrix, by rational incorporating manganese oxide active material, which is an ideal pseudo-capacitive material with high theoretical specific capacitance (1370 F g^{-1} for MnO_2). After the conformal deposition of manganese oxide nano-layer onto the FC-CNT surface, the original porous structure can be maintained. The 1) intrinsic high capacitance of manganese oxide, 2) highly porous structure, and 3) improved mass loading of active material (6 mg cm^{-2} for manganese oxide) are proven to facilitate the build-up of high specific energy on-chip supercapacitors.

2. Experimental

2.1. Electrode and device fabrication

Si NWAs with well-defined structure parameters were fabricated by a cyclic DRIE process, performed on an inductively coupled plasma system according to Ref. [5,6]. Nano-carbon films onto the Si NWAs were fabricated by our proposed template regulated compact integration strategy, in an atmospheric pressure chemical vapor deposition (CVD) process [4]. Afterwards, the DRIE Si NWAs supported nano-carbon films were employed as the matrix for manganese oxide growth. Specifically, the on-chip nano-carbon matrix samples were floated on 100 mL aqueous solution containing 2 mM $KMnO_4$ and 5 mM KOH in a beaker. Another beaker containing 100 mL 40–50 wt% hydrazine was placed adjacently. These two beakers were placed in a sealed container at room temperature. The volatile hydrazine as the reductant could diffuse into the aqueous solution, and further react with $KMnO_4$ to promote the growth of manganese oxide into the matrix.

2.2. Material characterization

Scanning electron microscopes (SEM, Hitachi SU-3500, 8230) equipped with electron dispersive X-ray (EDX) element analysis set-ups were employed to check the electrode structure and examine the element compositions of electrode samples.

2.3. Capacitor performance measurement

Three electrode half-cell, with Pt foil as the counter electrode, and Ag/AgCl (in saturated KCl) as the reference electrode were assembled first to characterize the electrochemical behaviour of single electrodes. Sandwich-type prototype supercapacitors with symmetric configuration were assembled for evaluating the energy and power densities. The employed electrolyte for both half-cell and full-cell measurement is 1 M Na_2SO_4 aqueous solution. Zahner IM6 electrochemical workstation was used for evaluation of the supercapacitor performance. Cyclic voltammograms (CV) and galvanostatic charge/discharge (GCD) techniques were adopted to measure the specific capacitance. Electrochemical impedance spectroscopy (EIS) was acquired over the frequency range from 10 mHz to 100 kHz with an AC perturbation of 10 mV at the open circuit potential.

3. Results and discussion

Figures 1a–b present that the surface of Si wafers was manufactured to NWAs after the DRIE process with a depth of 15–20 μm. The fabricated Si NWAs can be employed as structure templates to direct the compact assembly of cross-linked and interconnected FC-CNTs [4]. The highly porous structure of the obtained nano-carbon films has also been confirmed by our previous study. As displayed in 1c–d, the nano-carbon film is constructed with CNT units, and the NWA structured scaffold was buried under the compactly packed FC-CNTs (see inset rectangle in Figure 1d).

In this study, the conductive and porous carbon film on Si NWAs was adopted as an electrode matrix for loading high capacitance pseudo-capacitive manganese oxide. Figure 2 compares the introduced FC-CNT/Si NWAs matrix and the as obtained MnO_x/FC-CNT/Si NWAs via a facile chemical bath deposition (see Experimental section). Low magnification top-view SEM images (Figures 2a, d) show that the macroporous structure of the original FC-CNT film can be well maintained even with loaded MnO_x, which is beneficial to electrodes' supercapacitor application relying on favored electrolyte access. The conformal deposition of MnO_x layer is verified by high

magnification SEM characterization (Figures 2b, e). Stacked MnO_x nanosheets were grown conformally on the FC-CNT surface so that the one-dimensional structural feature of FC-CNTs was kept well after MnO_x loading. Figures 2c and 2f respectively present the cross sections of FC-CNT film and MnO_x/FC-CNT film. It can be found that the film thickness was kept almost unchanged, which confirms that MnO_x was definitely impregnated into the porous nano-carbon matrix rather than grown on the top of nano-carbon film, representing a conformal growth behaviour onto FC-CNTs. This uniform conformal growth and impregnation filling gave rise to a high mass loading of MnO_x active material (6 mg cm^{-2}), which is profitable for achieving high areal specific energy and is especially meaningful for on-chip application due to the limited footprint area for device construction.

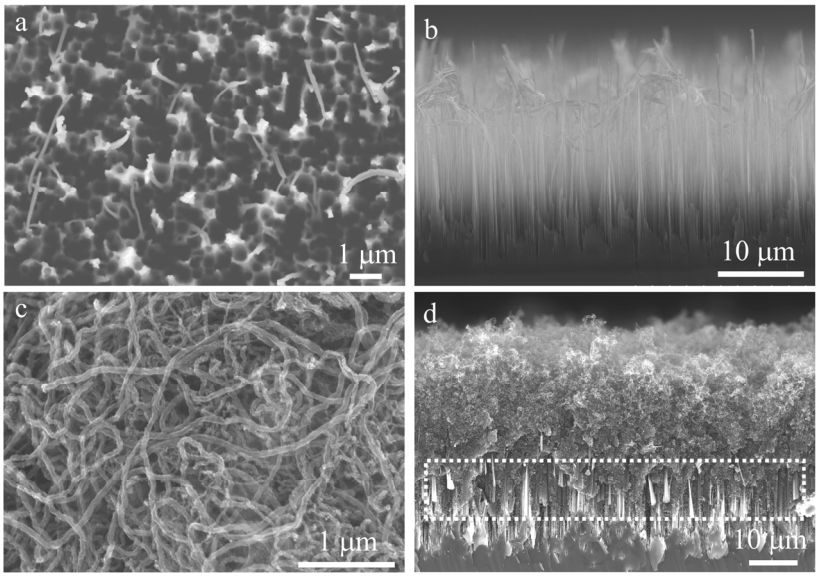

Figure 1. SEM images of (a–b) DRIE fabricated Si NWAs, (c–d) CVD deposited FC-CNT film onto the Si NWAs.

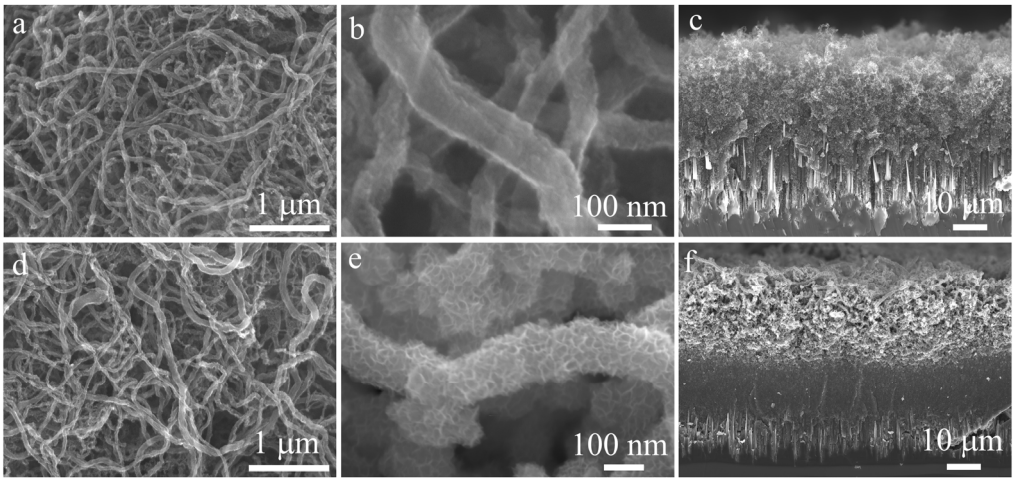

Figure 2. SEM images of (a–c) FC-CNT/Si NWAs matrix, (d–e) MnO_x/FC-CNT/Si NWAs.

The successful growth of MnO_x into the nano-carbon porous matrix can be further illuminated by the EDX analysis, as shown in Figure 3. Exclusive carbon element is verified in FC-CNT sample. The Si element from the underlying NWAs scaffold cannot be detected since the FC-CNT film on the Si NWAs is quite thick (30–40 μm) and compact. After the chemical bath deposition of MnO_x, besides carbon element, Mn, O, along with a small percentage of K were detected by EDX. It should be noted that trace K element is commonly included in solution chemistry prepared manganese oxide, in which K^+ is readily intercalated into the Mn-O layers [7].

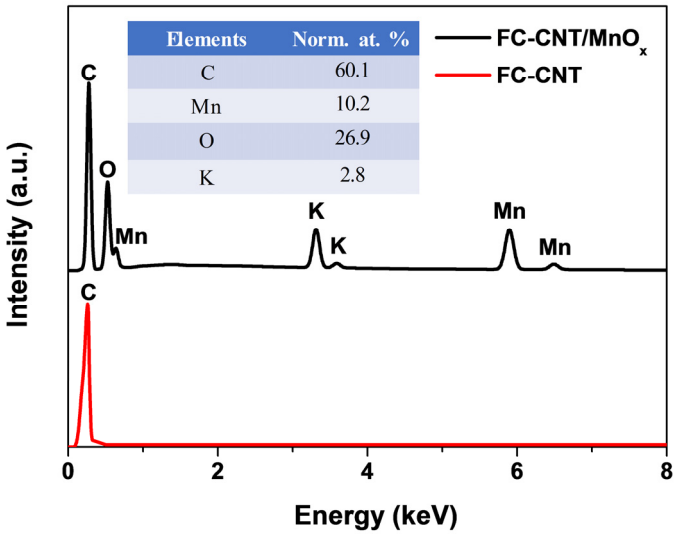

Figure 3. EDX results of FC-CNT and MnO_x/FC-CNT.

The performed material characterization proved that the obtained MnO_x/FC-CNT composite electrode inherited the highly porous structure of employed nano-carbon matrix. The good electric conductivity of the FC-CNT network is prone to help harvest the pseudo-capacitance of the deposited conformal layer of MnO_x. Meanwhile, a high areal mass loading of MnO_x active material would promise a high specific capacitance when applied in supercapacitors.

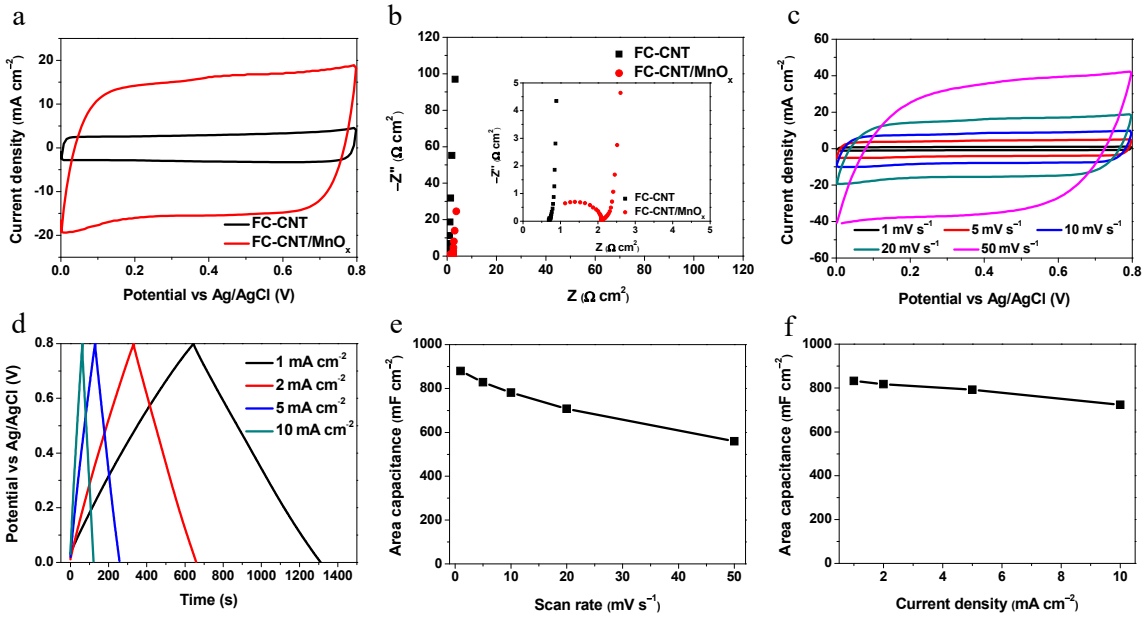

Figure 4. Half-cell capacitor performance of MnO_x/FC-CNT/Si NWAs electrodes.

Standard half-cell was first assembled for evaluating the electrochemical behaviour of the fabricated MnO_x/FC-CNT composite electrode. Figure 4a presents the rectangular shape of CV curve measured at 20 mV s^{-1}, which manifests the capacitor behaviour of MnO_x/FC-CNT electrode. The much larger integrated area of MnO_x/FC-CNT electrode corresponds to the higher specific capacitance of MnO_x/FC-CNT electrode than FC-CNT electrode by virtue of the pseudo-capacitive character of MnO_x. In the EIS measurement (Figure 4b), the semi-circle area in the high frequency range of MnO_x/FC-CNT electrode dictates the evident charge transfer resistance, which is normally observed in the pseudo-capacitive manganese oxide electrodes [8]. Both CV and GCD techniques performed at different charging/discharging rate were employed to evaluate the specific capacitance, as shown in Figures 4c–f. as high as 880 mF cm^{-2} could be delivered at a scanning rate of 1 mV^{-1}.

The good supercapacitor behaviour as verified in the half-cell measurement stimulated our further study on the performance of prototype devices. Figure 5 displays the electrochemical measurement results. Both the rectangular shape of CV curves (see Figure 5a) and symmetric triangular shape of GCD curves (see Figure 5b) exhibit a typical capacitor activity with a voltage range of 1 V. The assembled supercapacitor can offer a remarkable specific capacitance of 741.6 mF cm^{-2} when discharged at 1 mA cm^{-2}, normalized to single electrode. The specific energy of our prototype device is compared with reported representative manganese oxide based on-chip supercapacitors (Figure 5e). To the best of our knowledge, our supercapacitors are among the highest energy density systems. Figure 5f shows that the prototype device could work stably without any capacitance decay when scanned at 50 mV s^{-1} up to 5000 cycles.

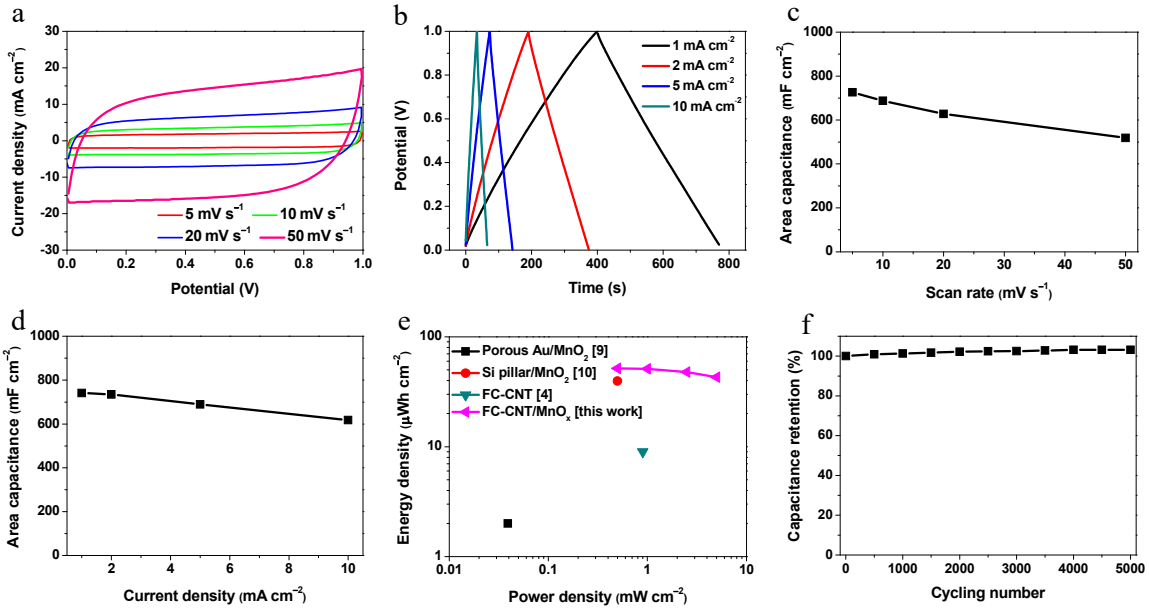

Figure 5. Full-cell capacitor performance of prototype on-chip devices based on MnO_x/FC-CNT/Si NWAs electrodes.

4. Conclusions

In this study, we proposed an on-chip supercapacitor electrode design, based on impregnating of pseudo-capacitive manganese oxide in the DRIE Si NWAs supported porous nano-carbon film. Benefiting from: 1) the intrinsic high capacitance of manganese oxide, 2) the well inherited highly porous structure from the original porous nano-carbon matrix, 3) the high level of mass loading of manganese oxide (6 mg cm^{-2}), and 4) the good conductivity of the employed nano-carbon matrix, the fabricated MnO_x/FC-CNT/Si-NWAs electrodes and prototype devices are proved to display high specific energy performance.

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