ABSTRACT

Three-dimensional (3D) supercapacitors have been demonstrated using vertically aligned carbon nanotubes (CNT) arrays and electroplated nickel nanoparticles. Two significant achievements have been demonstrated in this work: (1) a unique and reliable vacuum-assisted electroplating methodology for the uniform deposition of nickel nanoparticles on CNTs up to 150 μm in length, and (2) usage of pseudo capacitance to significantly enhance the energy density of CNT supercapacitors up to one order of magnitude higher than those without nickel nanoparticles coating. Experimental results show robust operation of more than 100 times charge/discharge tests.

INTRODUCTION

High power density supercapacitors with ultrathin and high energy storage capability are important for various applications. A typical supercapacitor contains three major parts: up and bottom charge-storage porous electrodes, ion-conductive electrolyte, and a separation layer in the middle, forming a typical sandwiched structure. The external electric field attracts positive and negative ions in the electrolyte to the electrode surfaces during the charging process. The opposite charges (electron or holes) establish a so-called electrochemical double layer at the interface. Supercapacitors bridge the power density and energy density gap between dielectric capacitors (high power but low energy density) and batteries (high energy but low power density) [1]. In general, supercapacitors use surface area rather than physical area of two electrodes to store charges. Electrodes with higher surface area can have larger charge storage capacity. Therefore, porous structures such as activated carbon are often used as electrodes in supercapacitors [2]. Furthermore, the ion charges stay at the surfaces of the electrodes in contrast to battery operations where ions go into the interior of the electrodes such as lithium-ion batteries. As a result, charges can be quickly stored and released in supercapacitors, resulting higher power density than batteries. Supercapacitors have very good stability and repeatability, typically 10^6 lifecycles about 10^3 cycles of lithium-ion batteries for pulse-power applications such as vehicle regenerative brakes and camera flashes.

Recently, researchers have begun to investigate new nanomaterials such as carbon nanotubes (CNTs) [3]. Compared to common electrode materials, CNTs have many advantages including high effective surface area, high conductivity, and no need of binder materials. Researchers have shown strong interests on vertically aligned carbon nanotube arrays [4]. Because of orderly aligned structure, vertically aligned CNT arrays have low contact resistance (each tube is individually connected to the substrate), high mass-to-volume ratio, and low ion transfer resistance (parallel channels between tubes) than randomly oriented CNT mats. However, limited energy density is one main drawback. To address this problem, the idea of pseudo-capacitors has been introduced, where additional bulk-charge-storage materials such as metal oxide (e.g. RuO_2, Ni(OH)₂) or conducting polymers are added into the electrodes [5]. This technique essentially adds the redox reaction similar to batteries. Figure 1 shows the mechanism of Ni(OH)₂ contributing to energy density on vertically aligned CNT arrays. In pseudo-capacitors, both surface-based electrochemical double layer and bulk-based materials contribute to the overall energy density to further increase the energy storage capability.
supply, energy storage, and on-chip component with large capacitance.

VACUUM-ASSISTED ELECTROPLATING

Nickel is used as the additional electrode material to demonstrate the pseudo capacitance [6]. Nickel will be oxidized as NiO(OH) during the supercapacitor operation and work as the cathode with the following reaction during the charging and discharging processes, respectively:

\[ \text{Ni(OH)}_2 + \text{OH}^- \rightleftharpoons \text{NiO(OH)} + \text{H}_2\text{O} + \text{e}^- \]  

(1)

Conventionally, nickel composite is mixed with activated carbon using sophisticated manufacturing steps [7]. In microfabrication processes, evaporation and sputtering can only reach a few micrometers into the dense CNT arrays [8] and won’t be suitable for the proposed supercapacitors. Because only the cathode is intended to be covered with nickel nanoparticles, we introduce a liquid-based, selective deposition process by means of electroplating.

Previously, researchers have only demonstrated electroplating on randomly distributed shallow CNT networks [9] and failed to make deposition on vertically aligned dense CNT arrays due to two major challenges. First, CNT is hydrophobic which prevents the wetting of electrolyte to the interior of CNT arrays. Second, high flow resistance caused by the densely-packed CNTs limits the ion transportation in electrolyte. Figure 2 shows the comparison of CNT arrays without electroplating in Fig. 2a and after the conventional electroplating (20s@40°C, 50mA/cm²) in Fig. 2b. A continuous Ni film has been deposited on the top surface as shown in the inset of Fig. 2b. However, cross-sectional SEM examinations reveal that only shallow penetration of nickel deposition as shown.

![Fig. 2. SEM photos of cross sectional views of (a) as-grown vertically aligned CNT arrays and (b) CNT arrays after conventional nickel electroplating process. Insets are the corresponding top views. Scale bars including insets are 200nm for (a) and 300nm for (b).](image)

We introduce here a simple, yet effective pressure-based electroplating method. The electrode with as-grown vertically aligned CNTs is placed into a chamber. Vacuum pump brings down the chamber pressure for 30mins or so. Deionized (DI) water is applied into the chamber in until the electrode is fully immersed in water and stay in water for about one hour. The chamber is vented and the electrodes are dipped into a big bath of electrolyte to replace DI water. Electroplating is conducted afterwards and Figure 3 shows the nickel deposition results using the proposed steps. It is observed that nickel nanoparticles are clearly visible from the cross sectional views of top, middle and bottom regions. This implies that the electroplating process successfully penetrate into the root of the dense CNT arrays. Nanoparticles instead of a continuous nickel film are deposited because electroplating process favors electrochemically active sites (e.g. defects and tips) [10].

The penetration of electrolyte within the vertically aligned CNT arrays is primarily determined by two factors: (1) properties of the interface between solid electrode and liquid, and (2) pressure differences. The first factor is not favorable since CNT is hydrophobic. The vacuum-assisted deposition process, on the other hand, effectively established a pressure difference of about 1atm which was found enough to push water into the vertically aligned CNT arrays.

![Fig. 3. 150µm-long vertically aligned CNTs after the vacuum-assisted electroplating process (4min@42°C, 50 mA/cm²). (a) Top view, (b)-(d) Cross sectional views of top, middle and bottom regions of CNTs, respectively. These cross sections were obtained by splitting fresh sample areas. (e) Global cross sectional view. The scale bars are 200nm for (a), 500nm for (b)-(d), and 20µm for (e).](image)
Figure 4 shows the statistical relationship between the nanoparticles size and electroplating time. It is observed that the size of nickel nanoparticles can be adjusted by controlling the electroplating time.

Several important processing steps are discussed:

1) DI water, instead of electroplating solution, is used in the vacuum infiltration process. The reason is that electrolyte used in nickel deposition can precipitate impurities under vacuum. Furthermore, cracks have been found in top view of CNTs as shown in Fig. 5a as compared with Fig. 5b where DI water is used with no observable cracks.

2) It is believed that two extra factors contributed to the uniform deposition of nickel nanoparticles in terms of size and density along the whole length of the CNTs. First, the voltage drop across the interface between the electrolyte and CNT electrodes is much larger than other potential drops. Therefore, the voltage drop along the length of the CNT is negligible for uniform deposition. Second, the total deposition time is short to have minimum impact on the local electrolyte concentration.

3) Some residual air can be trapped in the vertically aligned CNT arrays as some very small air bubbles were observed when DI water was added to the electrodes. However, these trapped air bubbles were observed to be rapidly dissolved during the venting process when the external pressure is applied onto these residual air bubbles.

EXPERIMENTAL RESULTS

These vertically aligned CNT arrays were synthesized using the process described before [11] to have about 150μm in height, 15nm in diameter, with an aspect ratio of about 10^4. Commercially available nickel electroplating solution (Technic, Inc., Cranston, RI) was used. These electrodes covered with nickel nanoparticles were thoroughly oxidized as NiO(OH) before usage [12] and a platinum wires was used as the counter electrode by using 0.1M NaOH as the electrolyte for the capacitance measurements via Reference 600™ Potentiostat (Gamry Instruments, Inc., Warminster, PA).

Figure 6 plotted the cyclic voltammetry curves of supercapacitor samples using “CNT+Ni” (blue), CNT (red), and Ni sheet (green) electrodes. Scanning rate was 100mV/sec@0.1M NaOH.

Figure 6 plotted the cyclic voltammetry curves of three supercapacitor samples using (1) CNT, (2) “Ni+CNT”, and (3)99.9% pure Ni sheet (preoxidized), respectively. Under similar voltage scanning rate and electrode area, the specific capacitance is proportional to the magnitude of current [1]. It is observed that “Ni+CNT” samples (blue line) have much higher outputs than both cases of CNT and nickel sheet samples. At the reducing peak of about -60mV, the transient capacitance of “Ni+CNT” sample was calculated as 26.7mF/cm^2, nearly one order of magnitude higher than the CNT case. It is also noted that the voltammetry curve of “Ni+CNT” deviated from
traditional rectangular shape (e.g. red line, CNT sample) with the peak-valley shape, indicating redox reaction indeed has happened. A close examination shows the “Ni+CNT” has much larger surrounded area compared with the Ni sheet sample. It further confirms that nickel redox reaction has occurred and “Ni+CNT” structure is better than pure Ni sheet electrode.

Figure 7a illustrates good cycling stability of our device by performing a charge/discharge test for over 100 cycles. Figure 7b shows the comparison between the very first five cycles and the final five cycles with good matches, indicating good repeatability during the charge/discharge cycles.

Fig. 7. Charge/discharge curves of nickel-functionalized CNT supercapacitors. (a) Data of the 100 cycle. (b) The first (green lines) and last five cycles (red lines). The experiments were carried out using 0.1M NaOH electrolyte.

CONCLUSIONS

Improved energy density of MEMS supercapacitors has been achieved utilizing vertically aligned CNT arrays with electroplated nickel nanoparticles. Uniform deposition of nickel nanoparticles was successfully developed using vacuum-assisted electroplating onto 150µm-high CNT arrays. These nickel-functionalized electrodes are measured to have maximum specific capacitance of 26.7mF/cm², nearly one order better than the one without coating of nickel nanoparticles. Good stability has been demonstrated during a 100-cycle charge/discharge test. As such, we think our vacuum-assisted deposition method can be applicable to various material systems and the demonstrated supercapacitor with higher energy density can be applicable to various electronics systems.

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REFERENCES