Laser Ablated Single Walled Carbon Nanotube Films as Microsupercapacitors

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Abstract

For the last decade carbon nanotubes (CNTs) are extensively investigated for many industrial areas thanks to their unique properties as a result of their novel structure. Their low resistivity, high electrochemical stability and high surface area are the foremost properties for their applicability in energy storage devices [1].

In this work, microsupercapacitors were directly patterned from single walled carbon nanotube (SWNT) buckypapers. These buckypapers were prepared using vacuum filtration and consecutive stamping method directly onto glass substrates. Patterning was performed via laser ablation technique, which eliminated the need for interdigitated contacts. Capacitive behaviour of SWNT microsupercapacitors were investigated through a galvanostat/potentiotstat using cyclic voltammetry, galvanostatic charge discharge and impedance spectroscopy techniques. An areal capacitance of 3.5 mF.cm⁻² was obtained through cyclic voltammetry at a scan rate of 10 mV/s using TBAPF₆:PMMA:PC:ACN gel electrolyte.

1. Introduction

Technological trend towards miniaturized electronic devices accelerated research towards improving energy density of micropower sources and small-scale energy storage devices. Short lifetime and limited power densities of small batteries hinders the further development of applications such as microelectromechanical systems, personal and military wearable technology and biosensors. As a replacement, electrochemical capacitors, or supercapacitors that have high power densities coupled with their excellent cyclability are offered for miniaturized electronic devices. However, current structures of supercapacitors must be enhanced in order to utilize them in microscale applications. In this manner, microsupercapacitors were investigated extensively [2].

Two different designs based on architecture exist for microsupercapacitors, namely interdigital in-plane architecture and three dimensional (3D) architecture. Thin film microsupercapacitors with interdigital in-plane architecture are generally preferred due to their scalability and low cost due to low amount of active materials [2]. While several techniques such as chemical vapor deposition [3], sputtering [4], in-situ chemical polymerization [5], electrochemical deposition [6] and inkjet printing [3] can be used to fabricate microsupercapacitor devices; graphene [7], activated carbon [8], CNTs [9], PANI [5], and MnO₂ [10] can be employed in this techniques as the active material. Among these materials, CNTs are good candidates for the fabrication of thin film microsupercapacitors due to their low resistance throughout the device provided by their percolation on top of their high surface area, stability and high electrochemical stability. However, aforementioned techniques generally require a pre- or post-processing for implementing interdigitated contacts. Herein, we report a fabrication route utilizing percolative CNT network to obtain a single step fabrication of microsupercapacitors offering low cost and scalability through laser ablation of the binder-free SWNT buckypapers on glass substrates.
2. Experimental Procedure

Sodium dodecylbenzenesulfonate (SDBS) and Tetrabutylammonium hexafluorophosphate (TBAPF6) is obtained from Sigma-Aldrich, and used without any further purification. SWNTs with an approximate diameter and length of 1.8 nm and 5 μm are obtained from TUBALL. PTFE membranes (JMWP04700, pore size of 5 μm) are obtained from Merck Millipore.

SWNT suspension is prepared using 1 gr of SDBS, 200 mL of isopropanol and 0.5 mg/mL of SWNT. Firstly, SDBS is dissolved in isopropanol via tip sonication for 5 minutes. Then, SWNTs are added to the SDBS/isopropanol solution and further tip sonicated for another 5 minutes. To prepare SWNT buckypapers on glass substrates, 10 mL of the prepared suspension is vacuum filtrated onto PTFE membranes and washed several times with isopropanol and DI water to get rid of SDBS. Afterwards, filtrated SWNT films was transferred onto glass substrates by adequate wetting with ethanol, and the membrane is lifted while the membrane is still wet. Resulting SWNT buckypaper film on the glass substrate was was dried at 50°C for 1 hour. The buckypaper film resistance after drying across the diameter (3.5 cm) is measured as 8 Ω.

SWNT buckypapers on glass substrates are patterned in two different ways for electrochemical performance comparison using EO Technics Laser Marker (50 μm spot size, 1064 nm wavelength, 30W power output at 100% power usage). First design consist of two electrodes patterned by separating the buckypaper into two with applying the laser marker as a line at 95% power output at 70 kHz frequency with 10 times sweeping. Second design consists of 24 electrodes with 12 micro-electrodes on each side, which was drawn beforehand in AutoCAD 2017 software and transferred to the laser marker software. For the second design, laser marker is applied again with the same power output and frequency with 40 times of sweeping. Buckypapers are further cleaned following patterning to remove residual materials. Final state of the patterned buckypapers can be seen in pictures provided in Figure 1.

3. Results and Discussion

Precise dimensions of the finger electrodes is obtained from SEM images provided in Figure 2. Average width of the finger electrodes, the gap created between them and the thickness of the electrodes are measured as 874 ± 1 μm, 112 ± 12 μm, and 13.5 ± 1.0 μm, respectively. The length of the finger electrodes are measured as 2.45 cm.

Figure 1. Photos of the laser ablated buckypapers with (a) a single line and (b) interdigitated finger electrodes. (c) AutoCAD 2017 was used for patterning in cm. (d) A photograph of the micro-supercapacitor cell prepared with TBAPF6:PMMA:PC:ACN gel electrolyte for electrochemical measurements.

Figure 2. SEM images of a microsupercapacitor fabricated with interdigitated finger electrodes using SWNT buckypapers. (a) Width of the electrodes and (b) width of laser ablated surface. (c) High magnification SEM image of laser ablated surface of SWNT buckypaper film. (d) Cross-sectional SEM image of one of the finger electrode.
Electrochemical characterization of the fabricated films are conducted using TBAPF6:PMMA:PC:ACN gel electrolyte with weight percentages of 3:7:20:70 by drop casting onto buckypapers. This device can be seen in Figure 1 (d). For both designs, electrochemical characterizations are made using cyclic voltammetry (CV), galvanostatic charge-discharge (GCD), and electrochemical impedance spectroscopy (EIS). Electrochemical characterizations of both designs and their comparison can be seen in Figure 3.

It is evident from the comparison in Figure 3 that the single line patterned buckypaper shows resistive behavior while interdigitated finger electrodes show promising capacitive behavior. This comparison shows the importance of electrode/electrolyte interface on the supercapacitive behavior.

The areal capacitance of the interdigitated finger electrodes are calculated from the formula below:

\[ C_{sp} = \frac{Q \Delta E}{A} \]

, where \( Q \) is the total charge passed (C), \( \Delta E \) is the voltage window (V), and \( A \) is the area of anode and cathode electrodes including the gaps between the finger electrodes (in cm\(^2\)). Effective area of the interdigitated finger electrodes is calculated from the dimensions obtained in Figure 2. From the CV measurement in Figure 3, areal capacitance of the interdigitated finger electrodes, or the fabricated microsupercapacitor, is found as 3.50 mF.cm\(^{-2}\).

From Figure 4 (a), areal capacitance of the microsupercapacitor is calculated as 3.13, 2.69, 2.26 and 1.81 mF.cm\(^{-2}\) for the scan rates of 20, 50, 100, and 200 mV/s, respectively. These results are highly comparable to those in literature and highly promising as a facile approach for the fabrication of microsupercapacitors [11,12].

3. Conclusions

To conclude, a facile and scalable approach to fabricate microsupercapacitors via preparing binder-free SWNT buckypapers on glass substrates via vacuum filtration method followed by laser ablation technique is achieved. Electrochemical performances of two different designs are evaluated and compared to show the importance of creating interdigitated micro-electrodes. An areal specific capacitance of 3.50 mF.cm\(^{-2}\) at a scan rate of 10 mV/s is obtained. Furthermore, a capacity retention up to 97% is attained at an applied current of 3 mA after 1000 charge-discharge cycles.
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References


