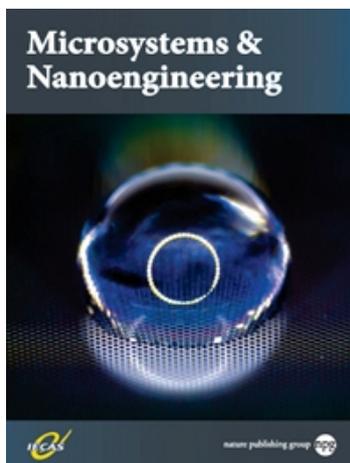


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Highly flexible, foldable and rollable microsupercapacitors on an ultrathin polyimide substrate with high power density

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Abstract

The design and functionality of extremely flexible, foldable, and rollable microsupercapacitors (MSCs) with in-plane interdigital electrodes that consist of single-walled carbon nanotube (SWCNT) networks on an ultrathin polyimide substrate are demonstrated through experiments and finite element simulations. The all-solid-state MSCs can be reversibly bent, folded, and rolled purely elastically without degradation of their electrical performance. The simulation results confirm that the deformation in bent, folded, and rolled MSCs is purely elastic. The high power density (1125 W cm^{-3}) and small time constant (1 ms) of the present MSCs are comparable to those of aluminum electrolytic capacitors. The MSCs operate at scan rates of up to 1000 V s^{-1} , are characterized by a volumetric capacitance of 18 F cm^{-3} and an energy density of 1.6 mWh cm^{-3} , and exhibit superior electrochemical stability with 96% capacity retention even after 100,000 charge/discharge cycles. The developed MSCs demonstrate high potential for integration in flexible and wearable electronic systems.

Keywords

Microsupercapacitors, single-walled carbon nanotubes, interdigital electrodes, finite element simulations, and flexible electronics

Introduction

Electric double-layer capacitors (EDLCs), also known as supercapacitors or ultracapacitors, rely on the rapid and reversible adsorption/desorption of ions at the electrode/electrolyte interface for charge storage. This kind of charge storage mechanism offers EDLCs several desirable properties, including long operation life ($>10,000$ cycles) and high power density. Typically, EDLCs deliver a power density about an order of magnitude higher than that of lithium-ion batteries and an energy density two orders of magnitude higher than that of electrolytic capacitors. Therefore, EDLCs could potentially replace traditional electrolytic capacitors to enable the further size reduction of electronic circuits.

The rapid growth of microscale flexible electronics, such as sensitive robotic skin [1], wearable photovoltaics [2], flexible transient electronics [3] and finger-tip devices [4], has increased the demand for microscale flexible energy-storage units, such as microsupercapacitors (MSCs). The MSCs with two-dimensional (2D) in-plane electrode structures have a lower device thickness than conventional supercapacitors with sandwiched electrodes, which not only endows the device with greater flexibility but also provides the potential to be folded and rolled to adapt to more applications. Moreover, because the ionic diffusion paths in 2D in-plane electrodes are much shorter, the rate capability and power performance of the devices can be greatly enhanced [5-7]. These properties are particularly important when the MSCs are coupled with microbatteries, microfuel cells, and energy harvesters to provide maximum power or when they are used to replace electrolytic capacitors in applications such as filtering voltage ripples in line-powered electronics (ac line filtering) [8,9].

Significant effort has focused on the design and fabrication of highly flexible and conductive electrodes with interconnected micro/nanostructures, such as carbide-derived carbon [10,11], carbon nanotubes [12,13], graphene [14–16], and graphene/carbon nanotube carpet [17]. Single-walled carbon nanotube (SWCNT) networks provide significantly higher conductivity, because the few interparticle contact yield a lower contact resistance than most other carbonaceous materials [18] used as electrode materials for high-power MSCs. Moreover, carbon nanotube (CNT) networks show superior robustness under bending, abrasion, and stretching, and their functionality is not affected by the development of mechanical stresses [19–23]. In addition, networks generally offer a high fault tolerance because many different current paths exist even with the presence of a few disconnected or missing links in the network. Various methods have been successfully developed to fabricate CNT networks for energy-storage applications, including vacuum filtration to form thick, free-standing membranes [24,25], mixing with a binder material [26,27], and electrophoretic deposition [13]. Although these methods can bring excellent electrochemical performance, wearable electronics impose increasing demands for energy-storage units with high-power behavior as well as foldability, rollability and stretchability. Dim et al. achieved stretchable MSC arrays with in-plane SWCNT electrodes using spray deposition [28]. The device showed stability under stretching and bending. We also previously reported stretchable MSC arrays with in-plane SWCNT electrodes fabricated on honeycomb PDMS substrates that exhibited good capacitive performance and excellent rate capability [29].

The objective of this study is to present a facile and scalable method of fabricating in-plane interdigital electrodes consisting of SWCNT networks by combining a simple spray-deposition technique with a single-step lift-off process. The produced SWCNT network is ultrathin, extremely flexible, and fully accessible by electrolyte ions during charging and discharging. The high flexibility and surface mountability of the present SWCNT MSCs are largely due to the ultrathin ($\sim 1.3 \mu\text{m}$ thick) polyimide (PI) substrate. Because of the high electrical conductivity of spray-coated SWCNT networks and the small space ($40 \mu\text{m}$) between the in-plane interdigital electrodes, the developed all-solid-state MSCs can operate at a high scan rate of 1000 V s^{-1} and demonstrate a volumetric capacitance of 18 F cm^{-3} , a maximum energy density of 1.6 mWh cm^{-3} , and a maximum power density of 1125 W cm^{-3} . Moreover, the present microdevices exhibit superior electrochemical stability (i.e., 96% capacity after 100,000 charge/discharge cycles), exceptional flexibility, and insignificant degradation in electrical performance even after excessive bending, folding, or rolling.

Materials and Methods

Spray deposition of SWCNT electrodes

Purified SWCNTs (P3-SWNT, Carbon Solutions) with 1–3 at% carboxylic acid surface functional groups were used as electrode materials. The SWCNTs were dispersed in deionized (DI) water with a tip sonicator for 1–2 h to form a 0.5–1 mg/ml stable suspension. The suspension was then sprayed onto a Si(100) wafer and placed onto a hotplate heated to 40–60 °C to form $\sim 140\text{-nm}$ -thick SWCNT films. The sprayed SWCNT films were used

as MSC electrodes without further treatment.

Preparation of gel electrolyte

The polymer electrolyte (PE) was prepared by mixing 10 ml of DI water with 10 ml of phosphoric acid (H_3PO_4) under magnetic stirring for 30 min and, separately, dissolving 10 g of polyvinyl alcohol (PVA) in 90 ml of DI water at 90 °C under magnetic stirring for 1 h. Finally, the two solutions were mixed under magnetic stirring for 1 h. The PVA: H_3PO_4 ratio in the PE was fixed at 1:1 wt/vol.

Fabrication of flexible SWCNT MSCs

MSCs with SWCNT electrodes were first fabricated on a Si(100) wafer by standard microfabrication techniques and, subsequently, carefully peeled off to obtain free-standing flexible MSCs. The first step of the fabrication process was to spin-coat a PI layer onto a Si(100) wafer (Supplementary Information, Fig. S1a). The PI solution (ZKPI-306II, POME Sci-tech, Beijing, China) was mixed with a PI thinner (POME Sci-tech, Beijing, China) in a weight ratio of 5:1 to form a diluted PI solution and then left overnight to allow the bubbles in the diluted PI solution to escape. Then, the diluted PI solution was spin-coated onto a Si(100) wafer in two steps (step 1: 800 rpm for 18 s and step 2: 6000 rpm for 60 s), soft baked in an oven at 80 °C for ~3 h for the solvent to evaporate, and cured in the oven at 250 °C for ~2 h. The PI film thickness was found to be ~1.3 μm . A bilayer consisting of an ~10-nm-thick Cr underlayer and an ~130-nm-thick Au top layer was evaporated onto the Si(100) wafer and patterned using a lift-off process to form the interdigital current collectors and contact pads of the MSCs (Fig. S1b). The lift-off process was performed in acetone under very gentle sonication. The SWCNTs were then spray-deposited onto the electrode area and patterned to interdigital electrodes by a lift-off process (Fig. S1c). The interdigital pattern of the SWCNT layer was the same as that of the underlying Cr/Au bilayer. For the lift-off process of the Cr/Au bilayer or the SWCNT layer, two layers of a photoresist film were spin-coated onto the substrates. The first photoresist layer (AR-P 5480, 100:50 dilution, Microchemicals) was spin-coated at 700 rpm for 9 s and at 2000 rpm for 40 s and then soft baked at 170 °C for 5 min. The second photoresist layer (AZ 601, Microchemicals) was spin-coated at 700 rpm for 9 s and at 3000 rpm for 40 s and then soft baked at 100 °C for 2 min. Finally, the two layers of the photoresist were exposed to UV light and developed. The fabricated devices were carefully peeled off the Si substrate (Fig. S1d) using the methods shown schematically in Fig. S2. Then, the PVA- H_3PO_4 gel electrolyte was coated onto the interdigital electrodes and left overnight at room temperature for the excess water to evaporate (Fig. S1e). Finally, a 10- to 20- μm -thick layer of polydimethylsiloxane (PDMS) was applied to encapsulate the microdevices (Fig. S1f). The PDMS resin and curing agent (10:1 weight ratio) were mixed for 5 min, degassed in a vacuum for ~30 min, carefully placed on the device surface, and finally cured at room temperature for ~24 h.

Characterization techniques

The microstructure of the sprayed SWCNTs was examined with a scanning electron microscope (SEM) (S-

5500, Hitachi, Tokyo, Japan). For cross-sectional SEM imaging, the microdevices were sectioned perpendicular to the finger length direction and coated with an ~1-nm-thick Au-Pd layer to enhance the surface conductance. To prepare samples for transmission electron microscope (TEM) imaging, the SWCNT powder was dispersed in DI water with a tip sonicator for ~2 h to form a 0.05 mg/ml stable suspension. Finally, a drop of the prepared suspension was applied to a standard Cu grid for imaging with the TEM (JEOL JEM2011, Peabody, Massachusetts, USA).

Electrochemical testing

The electrochemical performance of the SWCNT MSCs with the PVA-H₃PO₄ gel electrolyte was evaluated with a two-electrode system. Cyclic voltammograms (CV) and galvanostatic charge/discharge (GCD) experiments were performed with a CHI 860D electrochemical workstation. In the CV tests, the scan rate and voltage were varied in the range of 0.5–1000 V s⁻¹ and 0–0.8 V, respectively. In the GCD experiments, the microdevices were charged and discharged using a charge/discharge current of 10 nA cm⁻² and applying a voltage in the range of 0–0.8 V.

The volumetric capacitance C_v was determined from the CV response for scan rates in the range of 0.5–1000 V s⁻¹ using the relation

$$C_v = \frac{1}{\mathcal{V} \Delta V} \int I(t) dt \quad (1)$$

where ΔV is the potential range (= 0.8 V), \mathcal{V} is the total electrode volume (including the volume of the electrodes and interspace), $I(t)$ is the current measured during CV testing, and t is the time.

To determine the capacitance of the SWCNT layer, the capacitance of the Au current collector was subtracted from the total capacitance of the Au+SWCNT layers. In this paper, the MSC capacitance refers to that contributed only by the SWCNT electrodes.

The volumetric energy density E_V and power density P_V were calculated from the CV responses for a scan rate in the range of 0.5–1000 V s⁻¹ using the relations

$$E_V = \frac{1}{2} C_s \Delta V^2 / 3600 \quad (2)$$

$$P_V = \frac{1 C_s \Delta V^2}{2 t_d} \quad (3)$$

where t_d (in seconds) is the discharge time. The energy and power densities are those contributed by the SWCNT electrodes.

Electrochemical impedance spectroscopy (EIS) was performed by applying a 10 mV ac signal over the frequency range of 1–10⁶ Hz using an impedance/gain-phase analyzer (Solartron 1260, AMETEK Advanced Measurement Technology, Farnborough, Hampshire, UK). The real and imaginary parts of the impedance, Z' and